REVIEW OF OXIDATION AND SCALING OF HEATED SOLID METALS

PREFACE

THE Metallurgy Research Board of the Department of Scientific and Industrial Research has been engaged for some time past in bringing together as comprehensive a collection as possible of subjects which call for investigation and are thought to be of special importance to the metallurgical industries at the present time. Among the subjects which have thus been selected for special consideration is the study of the oxidation and scaling of heated solid metals.

This phenomenon is clearly one of great importance in the treatment, fabrication and use of metals. It involves the study of the mechanism and rate of oxidation of different metals and alloys in different atmospheres and the nature and properties of the oxide layers formed, as well as methods of preventing oxidation and of removing scale. The best plan of attack appeared to the Department to be to summon a conference of investigators, who had actually had occasion to deal with problems of oxidation and scaling in the course of their work, to discuss further action. The conclusion reached by the Conference was that, before any programme of future research could usefully be drawn up, it was very necessary to compile a full critical review of the recent work carried out on oxidation and scaling, in order to acquaint workers with the existing information on the subject and to provide a firm basis for proceeding to further investigations. Such a review is attempted in the sections which follow.

It was thought to be the most satisfactory arrangement to invite the various members of the conference (with such further expert assistance as they might consider desirable) to contribute separate sections dealing with those aspects of the subject which they were specially qualified to handle. A certain amount of overlapping has resulted, but this was inevitable in the circumstances and may perhaps be considered to be justifiable.

While the contributors to the Review have been mainly concerned to collect together and summarise the published

information upon oxidation and scaling, they have also taken the occasion to point out any aspects of the subject upon which existing knowledge is inadequate, and to draw attention to problems on which further research is necessary.

The Review is mainly concerned with the mechanism and rate of oxidation and the structure of the oxide layers; but the last two sections contain a description of the practical effects of oxidation and scaling, together with the methods to be employed for prevention.

Department of Scientific and Industrial Research,

16 Old Queen Street, Westminster, S.W.1.

June, 1935.

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REVIEW OF
OXIDATION AND SCALING OF
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SECTION I
THEORETICAL ASPECTS OF OXIDATION
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SURFACE FILMS

THE velocity of oxidation of metals is usually controlled by physical rather than chemical considerations, being limited by the rate at which oxygen and the metal come together. Given free access of oxygen, the chemical reactions appear to be rapid. Freundlich, Patscheke and Zocher [29] have shown optically that the mirror of pure iron, produced by the decomposition of the carbonyl, quickly undergoes superficial oxidation when exposed to dry air at ordinary temperature; but the oxidation ceases before the oxide becomes thick enough to be seen, presumably because the film prevents access of oxygen to the metal below. On *smooth* surfaces, the invisible film can be detected optically by the method developed by Tronstad[51], whilst the invisible oxide-film formed on *coarsely abraded* iron by exposure to air at ordinary temperature can be rendered visible to the eye by isolating it from the metallic basis; the isolation [18, 23] can be carried out by undermining the film with iodine or by anodic treatment, and the films are similar in appearance and composition to the thicker films obtained from iron which has been heated sufficiently to give interference tints. Vernon[54] has shown that copper exposed to air for an hour at 50° C. undergoes no visible change and very little increase of weight; but similar exposures at higher temperatures produce colour-changes and an increase of weight which rises rapidly with the temperature employed (0.04 mg/dm² at 100° C., 0·195 at 150° C. and 0.64 at 200° C.).

A study of the interference colours illustrates well this rapid increase of film-thickness with the temperature. Interference tints may usually be expected when the thickness of any oxide-film exceeds about 400 Å (obviously, the thickness at which the colours begin depends on the refractive index of the oxide, whilst the thickness beyond which they become inconspicuous depends mainly on the transparency); very thin films are usually invisible, whilst thick ones display the specific colour of the oxide. The colour produced by interference depends on the film thickness, and can be used as a rough method of measuring the latter. If a copper strip is heated at one end so as to produce a temperature gradient, no colours appear at the unheated end, the film being here too thin to be visible; but a fine sequence of interference tints appears as the heated end is approached. If the gas phase is only mildly oxidising, the colours, due to films of cuprous oxide, can be traced through four orders (i.e., red appears four times in the sequence); if a strongly oxidizing atmosphere is employed a " sooty " deposit of cupric oxide appears outside the cuprous oxide film, and obscures the colours beyond the middle of the second order.

These facts suggest that at low temperatures the oxide-film formed rapidly by the action of fairly dry, pure air on an ordinary metal is impervious to oxygen, and thus ceases to thicken before it reaches visible thickness; but that above a certain temperature (about 50° C. in the case of copper) oxygen can penetrate through the oxide to the metal below, and thus the film quickly attains sufficient thickness to become visible. Whether the temperature at which serious penetration of oxygen starts might, on some metals, be brought as low as " room temperature," seems doubtful; the rapid fouling of mercury rather suggests that this is the case, but it is still uncertain whether it occurs in pure oxygen. (According to R. S. Burdon[7] much of the contamination of mercury comes from the glass.) In any event, the example is an unsatisfactory one, in view of the liquid character of the basis. But there is no doubt that iodine can pass through iodide films, and sulphur compounds through sulphide films, without artificial heating. The action of air containing traces of hydrogen sulphide produces on copper the same sequence of tints at ordinary temperatures as are produced in pure air on heating.[16] Copper sulphide films are, however, pervious to oxygen, as

well as to sulphur, as shown by Vernon,[55, 56] who also found that although sulphur is an essential constituent of the tarnish film formed on copper at ordinary temperatures, the films contain much more oxide than sulphide.

The thickness of the oxide-film reached under any definite conditions depends on a number of factors, and the reader may be referred to an excellent paper by Portevin, Pretét and Jolivet.[41, 42, 43] But the factors which chiefly influence the result are three, namely (a) the temperature, (b) the time of exposure, and (c) the presence of gaseous bodies other than oxygen. The same tint can be obtained by a short exposure at a high temperature as by a long exposure at a low temperature. But whilst it is often impracticable to obtain a complete sequence of interference tints by heating specimens at a single temperature for different times, it is easy to obtain the complete sequence by heating the metal for a single period through a range of temperatures. The very marked effect of temperature on oxidation rate has excited surprise and occasioned much discussion. Some years ago, Dunn[10] argued that it " ruled out any mechanism of oxidation founded upon the passage of oxygen through discrete cracks or channels " and suggested that " an oxygen molecule can only pass a structural unit provided that this possesses at the moment energy greater than a critical value causing a loosening of the oxide structure at that point." He calculated the proportion of units having an energy not less than a critical value, E_0, to be $e^{-E_0/RT}$ where R is the gas constant and T the absolute temperature. This should be proportional to the reaction constant, K, and consequently the curve connecting $\log_e$ K and $1/T$ should be a straight line, which Dunn found experimentally to be the case.

Experiments carried out at relatively low temperature, upon the attack on silver by iodine dissolved in various organic liquids[22] in which the effects of four variables (time, temperature, concentration and solvent) were studied, led the experimenters to the conclusion that " the iodine diffuses through pores . . . in a sort of loose union with the silver iodide of the walls . . . a process intermediate in character between gaseous diffusion and diffusion in solid solution." In recent years, the view that penetration occurs by the " lateral diffusion " of molecules adsorbed upon the walls of pores or fissures has become widely held. Dunn,[14] referring to oxide films, has lately stated that lateral diffusion is probably

important at low temperatures, but that lattice diffusion undoubtedly occurs at high temperatures.

The theoretical aspects of lateral diffusion through cracks have been discussed by Lennard-Jones, and others,[34, 45] who associate the energy of activation with the diffusing *gas*, whereas Dunn associates the energy of activation with the *solid*. In lateral diffusion also, the velocity of the process will be determined mainly by $e^{-E_o/RT}$, representing the proportion of molecules which possess an energy greater than E_o (the critical energy needed to render a molecule capable of moving along the surface, instead of simply vibrating about a position of minimum potential energy). This proportion will be great or small according as RT is great or small compared to E_o. The temperature at which $RT = E_o$ can be regarded as the temperature at which penetration by lateral diffusion becomes important. For the passage of carbon monoxide into mica this occurs at 125 abs., that is at $-148°$ C.

Some recent work on the diffusion of gases through fused silica may here be quoted as indicating that more than one type of transport is possible. After an experimental study, Barrer[4] reaches the conclusion that " the diffusing gases can migrate according to two mechanisms. Helium, hydrogen and neon can pass through the ' lattice ' of fused silica at high temperatures. The heavy gases, oxygen, nitrogen and argon, migrate through slip-planes. At low temperatures helium, hydrogen and neon also show slip-plane diffusion. There is evidence that migration proceeds from the adsorbed layer, not directly from the gas phase." However, Alty,[1] after considering the passage of helium and neon through fused silica, suggests that there is diffusion of adsorbed atoms along narrow cracks, and that the gas atoms enter the cracks directly from the gas-phase rather than from the layer of gas adsorbed on the silica surface.

TIME-OXIDATION CURVES

The effect of *time* on the thickness of oxide-films on metal exposed to oxygen or air can be embodied in extremely simple laws. Pilling and Bedworth[40] have shown that it is possible to assign the majority of metals to two main classes, according to the relations existing between the densities of the metal and its oxide. The *first class* contains most of the *lighter metals* (except aluminium); in this class, a simple calculation from the densities shows that the metal occupies a volume greater

than that of the oxide which it can produce. Magnesium oxide occupies only 84 per cent. of the volume of the metal contained in it, whilst calcium oxide occupies only 78 per cent. Thus when calcium is heated in air, the oxidation of the surface layer yields an oxide layer which is necessarily porous, and will not seriously obstruct the passage of oxygen to the metal below. Consequently the oxidation continues without retardation, and the thickness of the film (y) produced at constant temperature is proportional to the time of heating (t), *i.e.* $y = k_1 t$. Metals of this class, like calcium and magnesium, may be said to " burn in air "; they are quite useless for practical service at elevated temperatures.

The metals of the *second class* are mostly *dense metals*, occupying a volume smaller than the uncompressed volume of the oxide. When such a metal (e.g. copper) is heated in air, the conversion of the surface to oxide yields a film which is non-porous, and which, being in a state of unnatural lateral compression, hinders the meeting of oxygen and metal. Under certain conditions, the rate of passage of oxygen inwards through this laterally compressed film (and likewise the rate of diffusion of metal outwards) will be inversely proportional to the thickness;* consequently if the velocity of oxidation is regulated by the meeting of oxygen and metal, the attack on the metal is given by the Tammann-Pilling-Bedworth parabolic equation :—

$$dy/dt = k_2/y, \text{ or } y^2 = 2k_2 t + K$$

Thus, *in the absence of complicating factors*, the rate of oxidation falls off with the time, and the continuously increasing protection afforded by the oxide-film to the metal makes this class of metals suitable for use at moderately high temperatures.

That the compressional stresses ·to which the protection is attributed have a real existence seems to be confirmed by the fact that the films, when stripped from the metal, have a marked tendency to curl. More definite evidence is given by the electron diffraction studies of the oxide films formed on zinc by Finch and Quarrell.[28] When formed at fairly low

* This simple derivation of the parabolic law is given by G. Tammann [47], and also by N. B. Pilling and R. E. Bedworth [40]. Several writers regard it as not very rigid. J. S. Dunn [11] obtains the same result by considering the oxygen-concentration C at depth y and time t. Clearly $\partial c/\partial t$ is proportional to $\partial^2 C/\partial y^2$; whence he proves that the total amount of oxygen passing through the surface is proportional to dt. A similar treatment is given by K. Heindlhofer and B. M. Larsen [31].

temperatures, the zinc oxide is " pseudo-morphic " after the metal and is in a state of compression in the direction parallel to the surface; this compression is compensated by an extension in the direction at right angles. On heating, the structure reverts to that characteristic of unstressed zinc oxide, and this may explain why zinc (notwithstanding the fact that the uncompressed oxide occupies 159 per cent. of the space of the metal contained in it) does not resist serious oxidation at high temperatures. Perhaps the volatility of the metal, may, however, play a part in the oxidation of strongly heated zinc. Certainly the results obtained by Tammann and Köster[48] in the range 390°–412° C. indicate the film to have some protective character, since the thickening rate falls off with the thickness; the measurements of Bangham and Stafford[2] confirm this point qualitatively, although there is disagreement regarding the equation connecting thickness and time. Moreover Dunn[12] has shown that brasses containing less than 80 per cent. of copper, when heated in air, form a zinc oxide film which has a considerable protective action, the oxidation-rate being only about one-eighth of that of the copper-rich brasses, whose oxide-film contains copper in the same proportions as the alloy.

Many authorities contend that the integration constant, K, of the equation given above should be zero, arguing that, since in the special case when t = o, y is zero, it may be concluded that K = o. This argument appears wrong; in the special case where y = o, dy/dt would be infinite, if the equation held good. But chemical considerations *alone* would prevent the infinitely rapid oxidation of film-free metal, and clearly it is not permissible to use this limiting case in the calculation of the integration constant. Actually it has been shown [22] experimentally, in the attack on silver by a chloroform solution of iodine (which obeys the parabolic law in the " interference colour range " of thickness), that K is not zero; moreover there is in this case a marked departure from the parabolic law at low thicknesses, where the film thickness is found to be more nearly proportional to the time than to the square root of the time. Vernon[55] had, at an earlier date, made similar observations on copper specimens exposed at ordinary temperature to an atmosphere containing traces of sulphur compounds; the time-corrosion curve is linear in the early stages but becomes parabolic later on. The time-oxidation curves given by

O. F. Hudson, Herbert, Ball, and Bucknall[32] for copper in air containing 0.1 hydrogen chloride at 400° C., and in "imitation fire-box atmospheres" at 260° C., show departure from the parabolic law near the origin.

Even in pure oxygen, or oxygen-nitrogen mixtures, Feitnecht [26] finds that y^2/t at first decreases with the time, ultimately becoming constant. He concludes that the parabolic law is not valid in the early stages, and attributes this largely to crystal-growth in the cuprous oxide layer. Wilkins[58], however, points out that Feitnecht's results accurately obey the equation

$$y^2 = 2k_2t + K$$

and that the apparent discrepancy is due to the assumption that K is zero. There are many reasons why K should not be zero. One reason, indicated by Wilkins, is that the copper already carries an oxide at the instant when $t = 0$; he mentions the possibility of leakage of oxygen through the walls during the process of heating in carbon dioxide, and the partial decomposition of that gas; it must not be forgotten that the invisible film formed at ordinary temperatures during the preparation of the specimens may have an appreciable influence on the results.

Pilling and Bedworth's derivation of their parabolic law is really based on the argument that the passage of oxygen through the film, and thus the rate of film-growth, is proportional to the concentration gradient. If C_o and C_I be the concentrations of excess oxygen (over and above the proper content of the oxide) at the outer and inner surface, then it may be argued by analogy with the heat-transfer equations that

$$\frac{dy}{dt} = \frac{C_o - C_I}{y} k_3$$

We may proceed to consider the special case when (1) C_o is maintained at a fixed value, namely the saturation value, and when (2) C_I is kept at a value low compared to C_o, or at a fixed value (*e.g.*, the lowest value capable of producing fresh oxidation to the metal). *When both these conditions are fulfilled*, we reach the Tammann-Pilling-Bedworth law—

$$dy/dt = k_2/y$$

In general, the two conditions will be fulfilled when the pressure is high enough to keep the outer surface saturated, and when

the film is thick enough to transmit oxygen so slowly that it is taken up by the metal as quickly as it arrives. Hence the parabolic law may be expected to hold good for fairly high pressures and fairly thick films, but not for very low pressures and very thin films; and this is found to be the case.

The *first* condition will fail to be fulfilled at very low pressures. The limiting pressure below which the parabolic law ceases to be valid depends naturally on the surface condition of the copper; Wilkins and Rideal [62] have found that, by "activation" of the surface, the limiting pressure can be raised 13 times, but that it is depressed again by sintering. Wilkins suggests that, at the limiting pressure, the grain boundaries at the surface of the cuprous oxide are just saturated with adsorbed oxygen. For any given gas pressure, the extent of saturation is dependent on the rate of removal of oxygen from the surface either (a) by evaporation into the gas phase or (b) by diffusion into the oxide-film along a grain-boundary. At constant temperature the evaporation-rate is constant, but the diffusion inwards depends on the extent of the grain-boundaries. Activation increases the extent of these boundaries, and consequently the increase of limiting pressure with activation is explained.

The *second* condition will fail to be fulfilled for very thin films, which would be able to let through oxygen more quickly than it could combine chemically with the metal; there must always be a departure from the parabolic law in the early stages of film-formation. The following has been suggested as a more general treatment of cases *above* the limiting pressure. [15] If C_s be the saturation value of the oxygen-concentration which is maintained on the outer surface of the film, and C^1 be the oxygen-concentration at the inner surface, then, in a steady state where rate of arrival of oxygen through the film is equal to the rate of combination with metal,

$$dy/dt = \frac{K_1 (C_s - C^1)}{y} = K_2 C^1$$

where K_1 is a physical constant connected with the diffusivity and K_2 a chemical constant; (it is assumed that the reaction is of the first order in respect to oxygen.) Eliminating C^1 we get

$$dy/dt = \frac{K_1 K_2}{K_1 + y K_2} C_s.$$

At very small thicknesses where yK_2 is small compared to K_1, this becomes $dy/dt = K_2C_s$, representing a straight line. At large thicknesses, where yK_2 is large compared to K_1, the equation becomes $dy/dt = \dfrac{K_1}{y} C_s$ (representing the Tammann-Pilling-Bedworth parabolic law). Thus the complete curve should be straight at very low thicknesses, but should conform to the Tammann-Pilling-Bedworth Law at greater thicknesses; this has been found to be true, as already stated, for low-temperature films produced on copper in polluted air, although other explanations have here been suggested.

Another cause of the failure of the Tammann-Pilling-Bedworth Law in the initial stages, pointed out by Wilkins, [59, 60] is the finite time taken to saturate the gas-solid interface. In the oxidation of copper, the parabolic law fails to hold over certain ranges of pressure during the initial stages simply because the oxide-oxygen interface has not reached the adsorption equilibrium.

Although the oxidation of copper appears explicable by assuming a simple movement of excess oxygen inwards through the oxide-film, the facts of the oxidation of iron—as established by the work of Pfeil [38]—require *also* the assumption of the diffusion of excess iron outwards through the oxide-scale. The matter is somewhat involved owing to the existence of three different oxide-layers on the metal. Notwithstanding these complications, the recent work of Portevin, Prétét and Jolivet [43] has shown that the parabolic law is very accurately obeyed by electrolytic iron between 825° and 1000°C, although there is an undoubted deviation from the law with some alloys, and earlier work* had seemed to indicate another law

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* According to G. Tammann, W. Köster, and G. Siebel [49] the film-thickness (y) on iron after time t in oxygen-nitrogen mixtures over the range 250-430°C., is given by the equation $t = ae^{by} - a$, where y is the oxide-film thickness at time t, and a and b are constants. Of these, b varies with the temperature and is different for different constituents such as ferrite, cementite, etc. They state that the same equation holds good for copper, nickel, zinc, cadmium, tin and lead, in partial contradiction with Dunn and others. Tammann measured the thickness by means of the interference colour, a method which U. R. Evans and L. C. Bannister [22] consider to be not always accurate. Dunn states [14] that Tammann and his colleagues omitted to take into account the fact that the light undergoes a phase-change both at the air-oxide and oxide-metal interfaces and adds that when this is allowed for, Tammann's observations lead to the parabolic law. However, in the case of iron, he states, the parabolic law does not hold at low temperatures.

for lower temperatures. The three layers are usually referred to as consisting of ferrous oxide, magnetite and ferric oxide respectively. Pfeil [39] has pointed out, however, that the lowest phase never corresponds to the exact composition FeO, and that a range of composition is possible in the other layers. Furthermore, the so-called "ferrous oxide" phase decomposes into iron and magnetite below 575°C, and in scale formed below that temperature, the ferrous oxide layer may be absent. This is a matter of some importance in the descaling of steel by means of acid, as shown by the work of Winterbottom and Reed [63]; ferrous oxide is much more readily soluble than the other oxides, and low-temperature scale, from which the ferrous oxide is absent, is much more difficult to remove by pickling. The decomposition of the ferrous phase may also account for the observation of Portevin, Prétét and Jolivet [44] that the ferrous oxide layer can be subdivided into two parts, the inner one homogeneous and the outer one containing crystals of magnetite embedded in the ferrous phase. Thus the structure of scale on iron is very complicated, especially when other elements are present, but our knowledge has been greatly extended by the valuable work of Pfeil, that of Portevin and his colleagues, and that of Jenkin, Winterbottom and Lewis. [32] Further reference should be made to the section of this report contributed by Dr. Pfeil and Mr. Winterbottom.

The deviation from the parabolic law met with in the alloys may be due partly to interaction between the oxide-film and the metal. Pfeil [67] found that iron-nickel alloy gave a scale with comparatively little nickel in the outer layers, but much free nickel, present as *metal*, in the inner layer; apparently both metals suffer oxidation, but the nickel oxide is then reduced by further iron giving the metallic nickel. Similarly Dunn's observation, already quoted, that brasses with less than 80 per cent. of copper give a scale of pure zinc oxide, is attributable to the reduction of the copper oxide by zinc diffusing up to the surface.

In addition to the two main classes of metals enumerated above, Pilling and Bedworth recognise other possible cases [40]. Molybdenum, for instance, has a volatile oxide which may sometimes evaporate as fast as it forms, leaving the metal clean. This only occurs in a stream of oxygen; Bannister, [3] working in closed tubes, has produced interference colours on molybdenum. Then again the noble metals, such as mercury,

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silver, platinum or gold, form oxides whose dissociation pressures reach the atmospheric value at rather low temperatures. Above these temperatures, no oxidation can be expected, unless increased oxygen pressure be employed; Pilling and Bedworth calculate that the dissociation pressure of silver oxide reaches atmospheric value at about 150°C. The oxidation of noble metals at low temperatures is not excluded by this argument, but it is by no means certain that all the oxygen molecules are capable of combining. Rideal and Wansbrough-Jones [46] state that those metals which possess a thermionic work-function exceeding 3·6 volts will combine only with molecules of sufficiently high energy content; the number of molecules possessing sufficient energy will clearly be proportional to $e^{-E_0/RT}$ (where E_0 is the energy required and T is the absolute temperature); the number may be very small at " ordinary " temperatures.

Particularly interesting is the behaviour of aluminium. Pilling and Bedworth [40] found that this metal, heated at 600°C, oxidized regularly for about 80 hours, and then suddenly, at a film-thickness of about 2×10^{-5} cms, the oxidation ceased, apparently owing to some sintering change in the film-substance, which became impervious. Cadmium showed the same behaviour at 300°C. Apparently the formation of layers which, even at very high temperatures, arrest almost completely the movement of oxygen inwards and metal outwards, is characteristic of certain alloys containing chromium. Tests by Utida and Saito [53] on wires of nickel-chromium alloys suggest that, with some compositions, a final state is gradually reached at which oxidation practically ceases; the parabolic law does not seem to account satisfactorily for the slowing up of corrosion, although part of the deviation can be attributed to the diminishing area of the metal as the wire suffers oxidation. It seems probable that, on some of these materials, sintering takes place continuously, converting the oxide to a form which, notwithstanding the high temperature employed, is practically impervious to oxygen. Of the seven alloys tested by Utida and Saito, the one which showed the highest velocity in the early stages seemed to suffer the least oxidation after six hours heating.

Most of the special alloys designed to withstand oxidation at high temperatures contain chromium or aluminium. Very interesting is the effect of adding aluminium and chromium to

iron and brass. Portevin, Prétét and Jolivet[43] found that the oxidation of pure iron at 825, 950 and 1000°C. obeyed the parabolic law, and that when an increasing quantity of aluminium was introduced into the iron, the time-oxidation curve, whilst retaining its general shape, was gradually shifted towards the time axis as the aluminium content was increased, indicating a retardation of corrosion; the addition of 7·4 per cent. of aluminium produced a remarkable resistance to oxygen at 900°C. Chromium produced a rather similar protective action, the effect of 13 per cent. chromium being much more striking than the effect of 6 per cent. chromium. Dunn's curves[13] on 70/30 brasses containing different quantities of aluminium showed similar shifts, but the additions needed to produce resistance were much smaller; each alloy gave a smooth time-oxidation curve, but the gradient was depressed as the aluminium content was increased, until at 1·9 per cent. of aluminium the oxidation-rate was only one-fortieth of that of aluminium-free brass.

CRACKING OF OXIDE FILMS

Since in general the protective action of a film increases with thickness, it might be argued that it is only a question of time before the protection becomes as complete as could be desired. Unfortunately this does not occur, owing to the tendency to cracking. One of the nickel-chromium alloys tested by Utida and Saito had a brittle film and, although it gave fairly favourable results in the early stages, it suffered much more oxidation than the others after 6 hours. Pilling and Bedworth[40] showed that copper wire in the range 800°–1000° C. oxidized normally according to the parabolic law, but that at lower temperatures, around 500°C., the oxidation-time curve obtained ceased to be smooth, and exhibited sudden rises, evidently representing a cracking of the film. Apparently different varieties behave differently; Dunn[11] who used foil instead of wire, found excellent agreement with the parabolic law for commercial copper at 209°C. and 284°C. Cracking is, however, a general phenomenon, and may affect changes at ordinary temperature. Vernon[57] exposed aluminium indoors in an unsaturated (somewhat impure) atmosphere at S. Kensington; the curve connecting weight and time was found to flatten out as the protective oxide-film completed itself over the surface, but then periodically a sudden rise would occur, owing to the cracking of the film.

In service, cracking and peeling of films is doubtless produced most often by bending or by alternate heating and cooling; obviously, to withstand such conditions, very special properties must be demanded. But *spontaneous* cracking due to the pent up stresses is possible, even in the absence of external stresses.[21] When the plane surface of a metal is converted to oxide, the volume changes will leave in the oxide-film a store of compressional energy; if a small area a of a film of thickness y is peeled off from the metal, the pent-up energy released is ayW_c, where W_c is the compressional energy per unit *volume*. But this peeling needs the performance of work equal to aW_A, where W_A is the adhesional work per unit area; additional work will be needed to break the film round the edges of the area to be peeled. But even if the film-substance possesses *no strength, spontaneous* cracking cannot occur until $ayW_c > aW_A$ or $y = W_A/W_c$; in other words spontaneous cracking is only possible above a certain limiting film-thickness. If allowance is made for the strength of the film (possibly also for the existence of stresses in the metal), theory suggests that spontaneous cracking is highly improbable below a certain thickness, but will become increasingly more frequent as the thickness is raised above this threshold value (since the strength of the film will vary from point to point, owing to crystalline configuration and other factors). Thus it is evident that the " expected leakage " of a film due to *individual cracks* will *increase* with the film-thickness (at a given temperature), whilst that due to *continuous porosity* will *decrease* with the thickness. The total expected leakage will presumably be minimal at a thickness just below that at which spontaneous cracking becomes possible, and it appears to be a fact that the protection due to a film often reaches a maximum at a certain thickness. Thus the protection of iron against iodine or against copper nitrate often appears to be maximal just below the interference colour range, whilst the protection of copper against silver nitrate is maximal about the same thickness.[17, 19] Where the temperature is not constant, the increase of plasticity due to rise in temperature may overcome the effect of increasing thickness. Thus copper oxide films produced at 900°C. are *less* prone to film-cracking than those formed at 500°C. The cracking of oxide-films on resistance wires is most serious when the wires are alternately heated and cooled; but this is doubtless largely due to stresses set up by the contraction

on cooling, the coefficients of expansion of the film and metallic basis being different. In some materials, transformation in the metal or its oxide on cooling provides additional risks of cracking.

Similar considerations may show why magnesium and other metals of the " porous film class " can remain unoxidised in dry air at ordinary temperatures. If the invisible film formed at ordinary temperatures was already porous, the metal should quickly be destroyed, unless it is assumed that only a small fraction of the oxygen molecules can attack the metal. Actually, however, it is likely that the film on magnesium—like the film on zinc, examined by Finch and Quarrell—is in an unnatural condition; but on magnesium the internal stress is presumably a lateral tension, instead of the lateral compression found on zinc. Only when a certain thickness is exceeded will internal stresses become sufficient to render the film porous, although evidently the thickness needed will be far less than that needed to produce peeling in a metal of the second class. Thus, at ordinary temperatures the film will protect the metal; but as soon as a temperature is reached at which diffusion through the film becomes appreciable, any additional thickening of the film will lead to a layer of porous, fluffy oxide, and the oxidation, once fairly started, will not fall off with the time.

STIMULATION OF OXIDATION BY ATMOSPHERIC IMPURITIES

The stimulation of the oxidation of ferrous material by the presence of gases such as sulphur dioxide, carbon dioxide and water vapour is most important. It occurs not only for ordinary steel, but also for heat-resisting steels containing chromium (usually also nickel and other elements). The measurements of Hatfield[30] on this point require detailed study. It seems likely that, in presence of such impurities, small traces of sulphates, carbonates and hydroxides are momentarily formed and quickly decomposed, leaving a certain amount of secondary oxide which will almost certainly be more porous than that formed directly from the metal;[20] even a mere trace of such secondary oxide will greatly reduce the shielding power of the oxide-film. On this point, the important work of Cobb and his colleagues[5, 6, 8, 9] now in progress may be expected to throw much light; already it has been found that the amount of scaling increases rapidly with the sulphur dioxide in the gas up to $0 \cdot 01$ per cent., and more slowly beyond this point. Sulphur can be detected in the metal and/or slag beyond the point in question. The extensive corrosion set up

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where the condensation of water containing sulphur acids occurs through the impingement of products of combustion on cold metal—an important matter in the coal-gas industry and in boilers—does not enter into the province of this review.

Heindlhofer and Larsen[31] report that the exposure of iron at high temperatures to carbon dioxide produces scaling somewhat less rapidly than exposure to air, whilst exposure to steam causes somewhat more rapid attack, owing to the more porous nature of the scale. The results of Upthegrove[52] at heat-treating temperatures are in general agreement as regards the relative dangers of air, oxygen, carbon dioxide, and water vapour, and the accelerating effect of traces of sulphur dioxide. The curves of Murphy and Jominy[35] at forging temperatures indicate that carbon dioxide may sometimes be almost as destructive as air; here again the effect of sulphur dioxide was marked, and steam was shown to oxidize steel more rapidly than air. Fells,[24] discussing the use of coal gas in the steel industry, recommends the reduction of the water content, by cooling the products of combustion of the gas; if, subsequently, a certain proportion of unburnt gas is added, the mixture can be regarded as non-scaling. Cobb has shown that the quantity of unburnt gas needed to render a gas-mixture non-scaling is much greater, if water-vapour be present in large quantities.

Much can be done to prevent scaling of ordinary steel by control of furnace atmosphere, but clearly this is not always possible and often resistant materials must be sought. The task confronting metallurgists is not the production of materials resistant when exposed to pure oxygen under constant temperature, but rather materials that will resist scaling when exposed to fluctuating temperatures, alternating stresses, and in an atmosphere rich in sulphur dioxide, carbon dioxide, water-vapour and other impurities. The mechanical properties at the temperature in question require to be satisfactory, and indeed the questions of mechanical and chemical deterioration require to considered together; deformation of the metal in the plastic range—perhaps even in the elastic range—involves a certain danger of rupture of the protective oxide film and may thus stimulate chemical attack; conversely chemical oxidation will increase the danger of mechanical failure.

In writing this introductory section I am indebted to Dr. J. S. Dunn, Dr. J. C. Hudson, Mr. A. B. Winterbottom, and others for numerous helpful suggestions.

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THE CONSTITUTION AND FORMATION OF SCALE ON FERROUS ALLOYS

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EQUILIBRIUM DIAGRAM

A KNOWLEDGE of the equilibrium diagram of the iron-oxygen system over the range FeO to Fe_2O_3 is of the first importance in the development of a thorough understanding of the fundamental principles of scaling of ferrous alloys. In chemical literature[51] as many as ten oxides of iron have been described, and although the results of recent researches have made it improbable that there are more than four phases between 70 and 77·73 per cent. iron (corresponding to Fe_2O_3 and FeO respectively) no equilibrium diagram has been produced which can be accepted as correct. Information bearing on the iron-oxygen equilibrium diagram may be obtained from a very large number of sources* and from six of these the attached diagram opposite has been produced.

Broadly speaking the solidus and liquidus curves reproduced in the diagram were obtained by carrying out cooling curves in platinum crucibles using a bare precious metal couple. For the most part the oxides employed were prepared using either electrolytic iron or ferrous oxalate as raw materials. A common procedure has been to produce two oxides, one saturated with oxygen and the other as nearly as possible saturated with iron, and from these two to make up mixtures for intermediate iron contents. In some cases, however, mixtures of ferric oxide and iron powder have been employed. As will be pointed out later, platinum at present appears to be the only satisfactory container for molten iron-oxide other than iron-oxide saturated with iron, for which pure iron containers are suitable. The molten oxide reacts readily with

* *See* references [3, 17, 18, 25, 27, 28, 32, 35, 43, 44, 45, 40, 69].

THE IRON OXYGEN EQUILIBRIUM DIAGRAM 70-78% IRON.

DEGREES CENTIGRADE

IRON PER CENT.
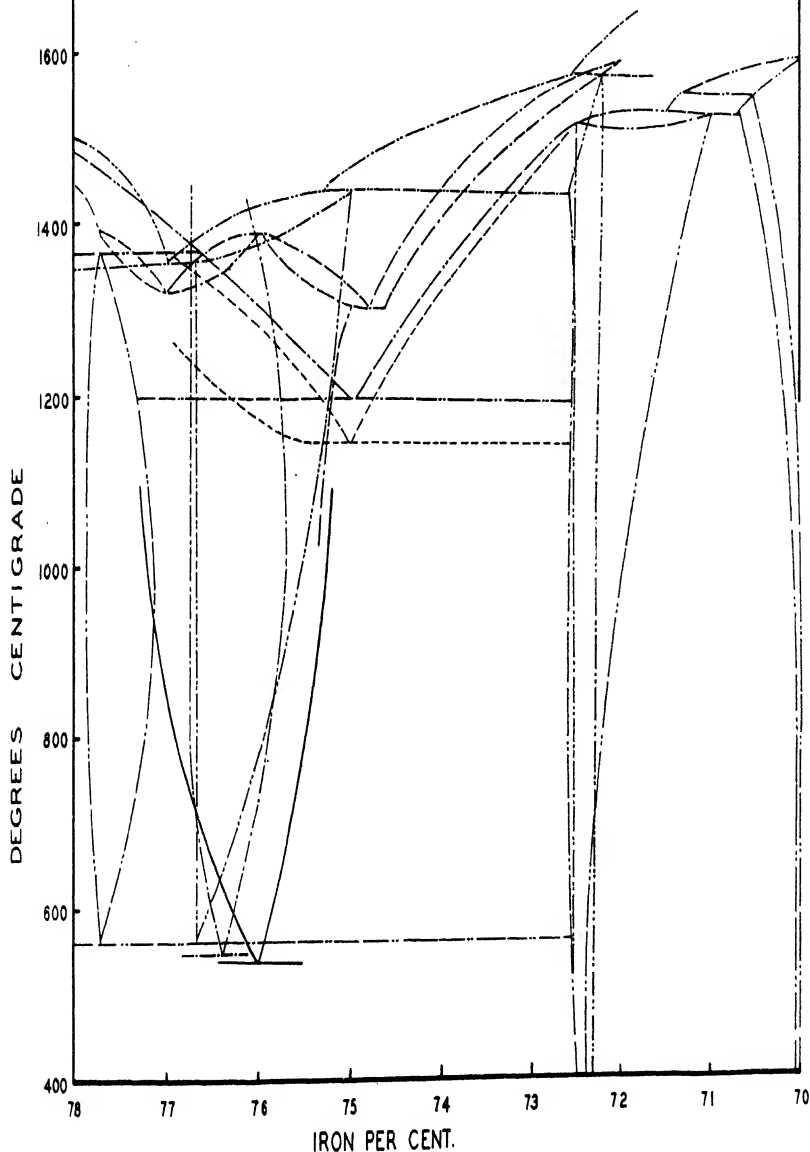
C. BENEDICKS. & H. LOFQUIST.
MATHEWSON, SPIRE, & MILLIGAN.
E.R. JETTE & F. FOOTE.
H. SCHENCK & E. HENGLER.
R. SCHENCK & T. DINGMANN.
L.B. PFEIL.

oxygen and precautions have been found necessary in order to avoid a change in composition during melting. In some cases this has been accomplished by melting in a nitrogen atmosphere and in other cases by melting in vacuo. Most workers appear to have analysed their samples after the completion of the cooling curve with the object of taking into account any changes in composition which took place during the taking of the curve.

It will be at once apparent from the diagrams shown superimposed, that remarkably varied results have been returned for the system during the past seven years. The results of various workers differ perhaps to the most marked extent in the section of the diagram covering the range 74 to 76 per cent. iron. In this range Mathewson and his collaborators have shown a melting point as low as 1150° C., while Pfeil obtained for the same composition a melting point of about 1450° C. H. Schenck and E. Hengler found an intermediate temperature of about 1300° C., while C. Benedicks and H. Löfquist drew their diagram to show a melting point of 1200° C. for oxide containing 75 per cent. iron. Not only are there these wide differences in opinion regarding the melting point in this region of the diagram, but in addition there is a difference of opinion as to whether a eutectic or a peritectic reaction exists in the system between Fe_3O_4 and FeO.

Doubts still remain as to whether the compound FeO has any real existence. According to Benedick's diagram this compound exists over a range of temperatures and is capable of dissolving small amounts of iron and of oxygen. The preparation of pure FeO has been described by Andrew and his collaborators[2] and by others[22, 60]. On the other hand experiments carried out by R. Schenck and T. Dingmann tended to suggest that this compound did not exist, while the diagram published by Pfeil excluded the compound FeO. Later work by Jette and Foote using X-ray methods led them to the conclusion that FeO had no real existence.

The position appears to be that there is no definite compound corresponding to FeO, but that the oxide phase richest in iron is a solid solution extending over the range of approximately 75 to 77 per cent. iron. This phase was named Wüstite by Schenck et al. after Geheimrat F. Wüst, an early director of the Kaiser Wilhelm Institute, Dusseldorf, and the term has been fairly generally adopted by subsequent investigators.

According to Jette and Foote this phase has a maximum solubility for oxygen at a temperature of 1100° C., but according to Pfeil a maximum solubility of oxygen at the melting point (about 1440°C.). According to Schenck and Dingmann's work this phase is capable of dissolving about 77.3 per cent. iron at 1100° C., but according to Pfeil and Jette and Foote the maximum solubility, which varies but little at temperatures over 800° C., is less than 77 per cent. iron (FeO 77.73 per cent. iron). There is general agreement that Wüstite decomposes at a temperature of about 570° C. into a eutectoid of metallic iron and magnetite. This transition is clearly indicated by the results of researches on the equilibria between Fe, C, H_2 and O_2.

Some further reference must be made to the differences of opinion regarding the existence of a eutectic at about the 75 per cent. iron level. Under the microscope specimens of about this iron content have an appearance such as might result from the existence of a eutectic in the system, and Wyckoff and Crittenden interpreted their results as showing the existence of a eutectic. Benedicks and Löfquist accepted this evidence, while Mathewson and his collaborators and also Schenck and Hengler brought forward evidence in support of the existence of the eutectic, although the eutectic temperature obtained in these three researches differed greatly.

An alternative explanation for the structures of specimens of a composition around the 75 per cent. iron level is that magnetite particles separate from the Wüstite solid solution on cooling and Pfeil claims to have observed the resolution of most of the magnetite in the specimens containing about 75 per cent. iron by quenching from a temperature below the solidus. It appears that at high temperatures the separation of magnetite occurs from relatively few centres leading to the formation of large particles, whereas at lower temperatures the precipitation is more distributed and consequently finer. The change over from the coarse form to the fine form is rather sudden, and thus an appearance is developed simulating primary crystals in a eutectic ground mass. Structures simulating a eutectic can also be obtained in scales produced by oxidation at temperatures below the solidus and subsequent cooling.

In the vicinity of the composition of magnetite (72.4 per cent. iron) agreement between various workers as to the position

* *See* references [6, 7, 8, 9, 11, 12, 13, 29, 38, 41, 42, 43, 47, 56, 57, 58]

of the liquidus is relatively close, although the diagrams show a difference of opinion as to the extent of the solubility of oxygen and of iron in magnetite. Little is known about the equilibrium diagram in the region of Fe_2O_3, It has been shown[3, 21, 51] that at high temperatures ferric oxide has a relatively high dissociation pressure and melting could not be obtained without decomposition except under considerable oxygen pressures.

The lack of agreement regarding the equilibrium diagram for the iron-oxide system may be attributed very largely to the many experimental difficulties which must be overcome if accurate results are to be obtained. All the well-known refractory materials, including magnesia and alumina, are attacked by molten iron-oxide and the purity of the melt is liable to be affected. The effect of impurities on the experimental results likely to be obtained in studies of the iron-oxygen system has been dealt with at some length by Benedicks and Löfquist[4]. In this paper it was pointed out how misleading dissociation pressure curves are likely to be when working with impure and heterogeneous oxide. The conclusion which Sosmann and Hostetter[51] reached regarding solid solutions in the composition range Fe_2O_3 was based on dissociation pressure curves and considerable doubts have been cast on the validity of these conclusions[49]. It has been pointed out that since ferric-oxide crystallises in the hexagonal system and magnetite in the cubic system it is unlikely that a continuous series of solid solutions can be formed between these two compounds. It seems not improbable that the curves obtained by Sosmann and Hostetter were influenced by heterogeneity in their specimens.

The most satisfactory material at present available as a container for experiments on iron-oxide at high temperatures is platinum, but under certain circumstances reactions may occur between iron-oxide and platinum[50]. It has been experienced, for example, that platinum is embrittled when heated in contact with iron-oxide in an atmosphere of low oxygen pressure and this is due to the formation of a solid solution of iron in platinum[25].

MICROSTRUCTURE

In various publications photomicrographs may be seen illustrating the structure of scale on iron and unalloyed

steel[10, 24, 35, 36, 48, 54, 55] In the more recent of these papers there has been general agreement that three layers containing up to four phases are to be seen in the scale produced on iron at high temperatures in an air atmosphere. A thin layer of ferric oxide followed by a rather thicker layer of magnetite occur on the outside, while the bulk of the scale deposit is made up of Wüstite phase more or less decomposed according to the rate of cooling. The ferric-oxide phase has a whiter appearance than the magnetite and both these phases resist etching more powerfully than the Wüstite phase. At the temperature of formation, scale can only consist of monophase layers ; the duplex structures seen in sections result from subsequent changes during cooling, such as changes in solubility and eutectoid decomposition. After ordinary rates of cooling the Wüstite phase contains particles of magnetite which are coarser in size towards the contact with the magnetite layer. Near the scale-steel interface the Wüstite has a porous character and this, accentuated by its fragility and state of strain, renders it difficult to prepare micro-sections of this portion of the deposit. When oxidation takes place in an atmosphere deficient in oxygen, scale deposits may be obtained in which only the Wüstite phase appears. In these circumstances the scale has an appearance different from that in which the ferric-oxide and magnetic-oxide layers are present. The matte surface of the latter type of scale is replaced by idiomorphic crystalline growths[34]. R. Griffiths[16, 26] has reported that oxidation in steam-air mixture results in a thinner layer of ferric-oxide than that produced in air.

In the case of scale produced at a temperature below 570° C. the Wüstite phase should be absent, since this phase is believed to be unstable below 570° C.[55], and the layer adjacent to the steel should consist of magnetite or ferric oxide.

MECHANISM OF SCALING

During the last few years a number of papers have been published dealing with the mechanism by which the oxidation of iron takes place. Many years ago J. E. Stead[52] drew attention to the peculiar nature of the scale deposit on a 25 per cent. nickel steel, pointing out that the scale was made up of two layers, an outer black portion containing no metallic particles, and an inner grey portion one of the constituents of which consisted of metallic particles containing 76 per cent.

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nickel. A somewhat similar observation was made by Dickenson[10] who also noted a layer formation in the scale on high speed steel. Stead interpreted his experimental results as showing that when the scale deposit was thin the oxidation was intense and the metal oxidised as a whole, but that later on differential oxidation occurred, the iron diffusing to the surface of the metallic core, and becoming oxidised, while the nickel remained in the metallic form.

Carpenter and Elam[5] drew attention to a very remarkable form of scale on iron which had been heated with copper in vacuo. Following up these observations Pfeil carried out a series of experiments on the oxidation of iron and steel, and attempted to explain the formation of scale layers of differing composition and the development of the crystalline scale reported by Carpenter and Elam, as well as other scaling phenomena, by the hypothesis that the oxidation of iron and steel did not proceed by a simple process of diffusion of oxygen through the scale layer but by countercurrent diffusion of oxygen inwards and iron outwards through the scale layer. Other workers in this field have found evidence in support of this hypothesis although concluding in some cases that some modification of the hypothesis is necessary[26, 30, 39].

This suggested mechanism would not demand an oxidation rate different from the parabolic relationship between time and degree of oxidation which has been established by a number of workers, but it does serve to explain a number of peculiarities encountered in the scaling of iron and iron-rich alloys. Amongst these peculiarities it is perhaps worth while drawing attention to the finding (1) that the scale on iron occurs in the form of three separable layers, (2) that in the case of iron alloys the relative proportions of iron and alloying elements in the various layers differ, in most cases, to a very pronounced extent, (3) that under certain circumstances idiomorphic scale crystals may develop at the surface of the scale, (4) that during the progress of oxidation foreign particles may become embedded within the scale, although at the temperature of oxidation the scale is not readily subject to plastic flow.

An exact knowledge of the constitution of scale and of the mechanism by which the scaling of iron proceeds is of the first importance. Winterbottom and Reed[55] in their work on the pickling of steel have thrown a good deal of light on this important operation by taking into account the structure of the

scale deposits. In connection with corrosion the characteristics of the scale deposit are of importance and this matter has already received consideration[1, 24]. Corrosion-fatigue too, where the corroding agent is a hot gas, as for example in super-heaters[15] and internal combustion engine valves[23], involves scaling under conditions possibly not regarded as dangerous from the point of view of scaling alone. In the manufacture of hot-rolled steel products and especially of sheet for purposes such as motor car bodies, scaling is important[16]. It is perhaps in the field of heat-resisting alloys, however, that fundamental information regarding the oxidation of iron is likely to be of the greatest value.

SCALE ON ALLOY STEELS

A number of published researches have dealt with the nature of the scale deposits on alloys of iron with chromium, aluminium, silicon and nickel, but a stage has not yet been reached where it is possible to deduce with any degree of certainty either the melting points of the scales or their con-stitution. The general indications are that small additions of alloying elements do not result in any fundamental change in the mechanism of oxidation, but in many cases the presence of alloy elements in iron results in a pronounced difference in the constitution of the scale deposits.

A simple example is to be found in the alloys of iron and nickel, in which oxidation of the iron only takes place[33], and nickel is to be found in the scale in the form of small metallic globules which consist in fact of a nickel-rich nickel-iron alloy[52] in equilibrium with the Wüstite ground mass. The nature of the scale on nickel steel may be looked upon as evidence strongly in favour of the countercurrent mechanism of oxida-tion. The outer portion of the scale deposit on nickel steel is completely free from nickel, while in the innermost layer the nickel to iron ratio is 2 to 3 times as great as in the original steel; nevertheless the unoxidised steel core contains no more nickel than the original steel. The facts are somewhat different from the situation described by Stead, and the absence of metallic particles in the outer scale layer is not due to intense oxidation in the early stages but to the absence of nickel in this layer.

In iron-chromium alloys the outer scale layers have a lower chromium-iron ratio than that in the original alloy, and the

chromium is concentrated in the inner scale layer[33]. The exact form in which it occurs in the Wüstite phase has not been established with certainty. It is known that solid solutions between ferric oxide and chromium sesquioxide can exist[14, 59] but nothing is known either regarding the composition limits of the ternary Wüstite phase, if one is formed next to the metal surface, as seems probable, or of the effect of other oxides on the W stite transition.

Most of the published experimental work on iron-chromium alloys has centred round scaling rates in various atmospheres which are outside the scope of these notes, but in some cases the results obtained have been discussed from a theoretical view point. Rickett and Wood[39] consider that iron-chromium alloys suffer attack by both oxygen and hydrogen sulphide by a countercurrent diffusion mechanism similar to that suggested by Pfeil for the oxidation of iron. The structure of scale on iron-chromium alloys has been dealt with by Rickett and Wood and also by Portevin and his collaborators[36]. In the paper by the latter workers photomicrographs were included illustrating the existence of an external layer of Fe_2O_3, an intermediate layer of Fe_3O_4 and an inner layer loaded and modified by chromium oxide.

Comparatively little is known regarding the constitution of the scale forming on iron-aluminium alloys, although recently a number of papers have been published bearing on this matter. Portevin and his collaborators[36] published photomicrographs of the scale found on an iron-aluminium alloy and traced the existence of layers of ferric-oxide, magnetite, and a complex inner layer having a eutectiferous structure. Interesting information regarding scale formation on iron-aluminium alloys has been provided by G. Sykes and J. W. Bampfylde[40, 53]. Two types of scale have to be taken into account. Under conditions where oxidation is rapid a dense black adherent scale is formed, while where oxidation is slow the oxide forms as a fine powder varying in colour· from red to white with increasing temperature and aluminium content. An X-ray photograph of the white powder showed that it consisted of aluminium oxide. These authors found that a concentration gradient could develop in the metal due to the preferential oxidation of aluminium at the surface.

The constitution of the scale formed on iron-silicon alloys is of considerable interest. In the case of steel containing 2 per

cent. silicon the outer scale layers are free from silicon, while the inner scale layer is enriched in silicon, and it appears that the silicon exists in this layer as an iron-silicate commonly having a eutectic configuration[33].

Portevin and his collaborators[36] included in their studies the microstructures of iron-silicon alloys and confirmed the absence of silicon in the ferric-oxide and magnetite layers and its concentration within the boundary of the original steel. They looked upon this concentration as evidence of the slow rate of diffusion of silicon in the scale compared with that of iron. Silicon is not very effective in decreasing the rate of oxidation of iron[36] but has been shown to have a valuable effect in improving the oxidation resistance of alloy steels[19].

Information regarding the characteristics of the scale formed on steel containing copper has been given by W. Radeker[37]. In this research three layers were found in the scale on copper-containing steels, the outer layer consisting of ferric-oxide. the middle layer of magnetic oxide, and an inner layer having a heterogeneous structure. Metallic copper was found in the inner scale layer when the copper content of the steel exceeded 0.5 per cent. Analytical determinations, however, showed that copper was also present in the outer layers although the concentration in the outer layers was generally less than in the inner layer. This finding was considered to indicate that copper was soluble in the three-scale layers. Radeker found, however, that the ratio of copper to iron in the scale was less than the ratio of copper to iron in the steel, indicating that the steel was enriched in copper. In this research attention was also given to the scaling characteristics of steels containing copper together with another alloying element. Nickel, chromium, molybdenum, vanadium, cobalt and titanium were taken into consideration.

Nickel, chromium, and titanium were found concentrated in the inner scale layer, although the outer scale layers were not entirely free from these elements. The results obtained with the cobalt steel were exceptional, in that the inner scale layer contained less cobalt than the outer layers. The results obtained with the steel containing vanadium were also remarkable, in that the vanadium concentration was at a minimum in the middle scale layer.

Radeker discussed in detail the relationship between the

scaling characteristics of the steels and their susceptibility to cracking in the hot bend test.

The scaling characteristics of steels containing copper have also received attention from F. Nehl[31] and he too like Radeker and others[24] records the observation of a copper rich metallic phase at the steel surface and in the inner scale layers of copper bearing steels.

Of the other elements commonly present in steel manganese and tungsten tend to be concentrated in the inner scale layer, but the concentration, especially in the case of manganese, is by no means so complete as in the case of nickel and silicon[33]. The nature of the scale deposits on alloy steels containing manganese and tungsten has received but little attention. The iron-oxygen-manganese system had been studied[2, 20] and the existence of a continuous series of solid solutions from FeO to MnO has been reported. Solid solutions between Fe_2O_3 and MnO have also been found and it is not unlikely that the more uniform distribution of manganese through the scale as compared with the distribution of other alloying elements is due essentially to the capacity of the three iron oxide phases to dissolve manganese readily.

From these experimental results it may be concluded that the distribution of an alloy element in the scale is not a function of its affinity for oxygen, and it seems most probable that the distribution is due to the relative rates of diffusion of iron and the alloy element in the scale deposit. If this be the case it would follow that nickel and silicon have a negligible capacity for diffusion in the scale, while chromium, manganese, tungsten, and vanadium are able to diffuse to some extent but not so rapidly as iron.

It is of interest to speculate as to what the position would be were the composition of a steel such that the whole of the scale deposit, or the whole of one layer of the deposit, consisted of a phase such as ferrous silicate, of a compound such as chromite or of a complex make up of constituents such as ferrous silicate, chromite and nickel in which free iron oxide was absent. It may reasonably be anticipated that under some such circumstances the mechanism of oxidation would be different from that in the case of pure iron, owing to a change in the capacity for interdiffusion between iron and oxygen.

Quantitative experimental work on rates of oxidation indicates that the alloying elements commonly used in steel

manufacture to develop heat-resisting properties have a progressive effect, the rate of scaling decreasing gradually as the amount of the alloying element is increased. Results of this kind suggest that the rate of diffusion of oxygen or of iron in the scale deposit is gradually lessened owing to the blocking of the diffusion path. This may result merely from the presence of foreign atoms in the Wüstite lattice, but may be due also to the gradual replacement of the Wüstite by a phase through which iron and oxygen cannot diffuse.

It has frequently been observed that, when alloys having a high oxidation resistance are subject to prolonged oxidation at elevated temperatures, there is a pronounced tendency for the development of localised attack, the major portion of the surface being covered only by a thin oxide film, while in a few places severe attack develops, leading to wart-like protuberances of scale. Attack of this kind may be due to the incidence of the interdiffusion process of oxidation in a few places where the concentration of alloying elements in the steel is too low to develop a scale through which iron and oxygen cannot diffuse. Apart from causes inherent in the steel, it is also conceivable that external conditions may sometimes be such as to prevent locally the formation of protective scale, with the result that oxidation there proceeds unimpeded leading to the formation of a wart, reminiscent in appearance of the aggregation of corrosion products at the mouth of a corrosive pit. This possibly implies that the protective value of scales on steels exhibiting this phenomenon is chiefly resident in the outer oxygen-rich layers. The action of traces of SO_2 and other gases in stimulating scaling is also in keeping with the idea that the outer scale layer exerts a determining influence on the progress of scaling.

In practice interest in heat-resisting steels centres largely round the behaviour of the alloys in complex atmospheres. In industrial furnace atmospheres attack may be much more rapid than in air. This is common where the furnace atmosphere contains sulphur compounds. It has been shown, however, that the presence of steam may increase the rate of oxidation over that in air. Little is known about the mechanism of attack of iron and ferrous alloys in sulphur-containing atmospheres, although there have been a number of papers in recent years bearing on this problem.

It will be seen that there is a vast field open for research in

elucidating the constitution of the scales forming on alloy steels, and in studying the mechanism of scaling of alloy steels. Further, more information is required regarding the scaling of iron in atmospheres of a complex character and particularly in atmospheres containing steam and sulphur compounds, while fundamental studies are required of the scaling of alloy steels in complex atmospheres of the types existing in industry.

In the alloy steel field published information on scaling resistance lags far behind industrial developments. Alloy steels and alloy cast irons have been developed and are used in large quantities for furnace and other parts, but it is probable that substantial improvements in scaling resistance, combined with better mechanical and other properties, would quickly follow were sufficient information available to give a lead as to the best directions in which to proceed.

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QUANTITATIVE ASPECTS OF THE OXIDATION AND SCALING OF IRON AND STEEL AT ELEVATED TEMPERATURES

By J. C. Hudson, D.Sc., and T. E. Rooney

Introduction

We propose in this section of the report to give a short review of present knowledge · concerning the quantitative aspects of the oxidation and scaling of iron and steel at elevated temperatures, *i.e.*, of the variation in the degree of oxidation with temperature, time, the composition of the atmosphere and certain other factors. We shall, however, refrain from any detailed discussion of the effect of differences in the composition of the metal on the rate of oxidation for two reasons :—

(1) In the case of alloying elements deliberately added to reduce the oxidation rate, the resulting steels are to be classed as heat resisting steels and are considered in another section of this Report.

(2) In the case of the elements invariably present in all steels and of those elements added in relatively small amounts for other purposes than conferring heat resistance, *e.g.*, as in high tensile structural steels, we feel that, although some evidence as to their probable effect on the oxidation rate is undoubtedly to be found in the literature, a more systematic study of each case is desirable before any generalization is made.

We do not propose, therefore, to give a detailed synopsis of the many papers dealing with isolated parts of the subject or having an indirect bearing on it but rather to present a brief account of the few major researches specifically directed to the quantitative study of the oxidation of iron and steel, under controlled conditions. These researches are as follows :—

1922. J. H. S. Dickenson. A note on the scaling of heated steels[3].

1923. N. B. Pilling and R. E. Bedworth. The oxidation of metals at high temperatures[10]. (An earlier but less

complete account of this work was published in 1922[9].

1925. Y. UTIDA and M. SAITO. The oxidation of metals and alloys at high temperatures[15].

1927. W. H. HATFIELD. Heat resisting steels[4].

1927. J. W. COBB. The influence of atmosphere and temperature upon the scaling of steel. Part I (with C. B. MARSON). Scaling by air, water vapour and carbon dioxide. Part II (with H. T. ANGUS). Prevention of scaling by hydrogen and carbon monoxide[2].

1930. W. H. BLACKBURN and J. W. COBB. The influence of atmosphere on the scaling of mild steel[1].

1931. D. W. MURPHY and W. E. JOMINY. The influence of atmosphere and of temperature on the behaviour of steel in forging furnaces[8].

1932. W. SCHROEDER. Researches on the effects of time, temperature, gas velocity and atmosphere on the scaling of iron[12].

1933. C. UPTHEGROVE. Scaling of steel at heat treating temperatures[14].

1933. K. HEINDLHOFER and B. M. LARSEN. Rates of scale formation on iron and a few of its alloys[5].

1934. A. PORTEVIN, E. PRÉTÉT and H. JOLIVET. Methods for the study of the corrosion of metals and alloys by gases at elevated temperatures and the application thereof[11].

The most detailed investigations yet made in any one laboratory are probably those of Upthegrove, Murphy and Jominy, conducted in the Engineering Laboratories of the University of Michigan at the instigation of the American Gas Association. We shall, therefore, commence by considering the results of their work, then deal with the other major investigations, as supporting or modifying the results of these American workers, and finally endeavour to give a short summary of the general conclusions that may be drawn from the various investigations considered as a whole.

RESEARCHES OF UPTHEGROVE, MURPHY AND JOMINY

Although the paper by Murphy and Jominy[8] contains valuable information on the oxidation of steel in forging

furnaces, which is summarised at the end of this sub-section, the most important of the whole series of researches is that of Upthegrove[13], who made a systematic study of the oxidation of various steels in the pure gases, oxygen, air, carbon dioxide and steam, and also in various combustion atmospheres, at temperatures ranging from 540° to 1260° C. in individual cases. The effects of time, velocity of the gas stream and of the reduced partial pressures of the oxidising agent resulting from dilution with nitrogen were also investigated.

The tests were made on cylinders 2·5 in. long by $\frac{5}{8}$ in. diameter, polished on 00 emery, suitably degreased, and heated in a stream of the gas under investigation in a tube furnace. At the conclusion of the test the sample was withdrawn in a stream of nitrogen and quenched; this had the effect of loosening the scale in most cases and any residual scale was removed by electrolytic pickling. In general the weight of scale formed and the loss in weight of the specimen were determined. Each determination was made at least in duplicate and it may be noted that the agreement between duplicates is very good, pointing to careful and accurate work. Thus the losses in weight of four specimens heated in oxygen at 1093° C. were 0·3730, 0·3755, 0·3749 and 0·3759 lb. per 100 sq. in. respectively.

The results of a series of tests made on 0.15% carbon steel in a stream of each of the four pure gases, may be summarised thus :—

(1) Under the standardised experimental conditions, exposure for two hours at the temperature under investigation, the rate of gas flow being maintained at 30 ft. per minute— oxidation became appreciable at the following approximate temperatures : oxygen 700° C., air 670° C., carbon dioxide and steam 600° C. These are the temperatures at which the observed loss in weight was about 0·0028 lb. per 100 sq. in., equivalent to an oxidation of 0·0001 in. of metal.

(2) Apart from certain anomalies, which will be referred to later, the rate of oxidation increased slowly with temperature up to 925° C. in carbon dioxide but more rapidly in each of the other three gases. This is illustrated by the following approximate temperatures at which a loss equivalent to about 0·001 in. of metal occurred : carbon dioxide 1010° C., air and oxygen 850° C., steam 790° C; the corresponding thickness of the scale is of the same order of magnitude as

that remaining on structural iron and steel after commercial hot-rolling operations.

(3) At the highest temperature at which the tests were made in all the gases (1093° C.) steam proved the most corrosive of the four, the losses in weight being as follows :—

Atmosphere.	Loss in weight (lb./100 sq. in.)	Equivalent loss of metal (in.)
Carbon dioxide... ...	0·140	0·0049
Dry air	0·147	0·0052
Oxygen	0·375	0·0132
Steam	0·413	0·0145

(4) The general variation with temperature of the rate of attack in the different atmospheres will be gathered from the preceding data but it should be added that a smooth loss in weight/temperature curve was only obtained in the case of steam. Anomalies were observed in all other cases. Thus maximum and minimum values for the rate of oxidation were observed at about 980° and 1100° C. respectively in the case of air and at 760° and 830° C. in that of carbon dioxide, whilst the curve for oxygen showed a definite discontinuity at 980° C., the increase in the oxidation rate with temperature being less marked above this point. Analyses of the various oxide films showed that these peculiarities in the oxidation rates in air, oxygen and carbon dioxide were related to variations in the chemical composition of the scale, the ferrous iron content of which was found to be a maximum and a minimum respectively at the maximum and minimum points of the oxidation/temperature curves. Moreover, the breaks observed at 980° C. in the air and oxygen curve were associated with the appearance of blisters in the scale, causing it to lose contact with the metal and thus presumably interfering with the diffusion processes by which oxidation is generally believed to proceed.

(5) No definite relationship was found between the chemical composition of the scale and the ease with which it split off on quenching. It was noticed, however, that scales formed in air and oxygen at temperatures from 700° to 1100° C. were split off readily and that less than 10 per cent. adhered to the steel, whereas scale formed in steam at temperatures up to 980° C. was retained in excess of 80 per cent.; in the latter case the amount of scale adhering to the steel grew progressively less above 980° C. Scales formed in carbon dioxide varied widely

in their tendencies to split off but adhered less tenaciously than those formed in water vapour.

(6) The effect of variation in the time of heating at a constant temperature, up to a period of 5 or 8 hours was investigated for each of the four pure gases, with the following results :—

(i) In carbon dioxide the loss in weight at both 750° and 830° C. was practically proportional to the time of heating up to five hours.

(ii) The rate of oxidation in air and oxygen decreased rapidly over the first hour's exposure but then remained practically constant. This applies to experiments in air at 830° and 930° C. and in oxygen at 830° C., in which the loss in weight/time curves are to all intents and purposes straight lines between 2 and 5 hours' exposure. Of the three curves, that obtained in air at 830° C. could alone be reasonably well represented by a true parabola.

(iii) In steam at 930° C. there was only a slight falling off in the rate of attack over a period of 8 hours.

(7) A series of tests in which the partial pressure of the oxidising gas was reduced by dilution with nitrogen showed that :—

(i) In air and oxygen at 930° C., the effect of the diluent nitrogen is not appreciable until the oxygen content is reduced below 20 per cent.

(ii) Dilution of steam with nitrogen at 930° C. reduced the degree of scaling very rapidly for concentrations below 80 per cent. of steam.

(iii) In the case of carbon dioxide-nitrogen mixtures at 750° C., the degree of attack fell slowly with increasing nitrogen content to half its original value when 80 per cent. of nitrogen was present; further nitrogen additions had a more pronounced effect in reducing oxidation.

(iv) In mixtures of carbon dioxide and steam the scaling increased continuously with increasing concentration of the steam.

(8) The effect of variation in the rate of flow of the gas stream was studied at 750°, 830° and 930° C. In all cases other than that of oxygen at 830° C. a minimum rate of flow was found below which scaling decreased very rapidly and above which the increased rates had very little effect. Under the given experimental conditions the critical rate appeared to be about

$\frac{1}{2}$ ft. per minute for carbon dioxide at 750° C. and 5 ft. per minute for air and steam at 930° C. and to increase with temperature. [Upthegrove selected a speed of 30 ft. per minute for his main experimental work.]

Further oxidation studies were made under slightly modified experimental conditions, in gas combustion atmospheres, both on 0·15 per cent. carbon steel at 760° to 1040° C. and on a number of carbon and alloy steels at 930° C. Additional tests were also conducted on the effect of introducing a small percentage of sulphur dioxide into the gas.

In the case of 0·15 per cent. carbon steel, the scaling losses at 760° and 820° C. were found to be small, regardless of the type of atmosphere. The results showed that at these temperatures oxidation can be appreciably reduced by the presence of small percentages of carbon monoxide in the atmosphere; as the temperature increased very much higher percentages of carbon monoxide were necessary to effect corresponding reductions. Thus, under the given experimental conditions, from one to two per cent. of carbon monoxide proved sufficient to reduce the scaling loss below 0·03 lb. per sq. in. at temperatures up to 930° C., whereas at 1040° C. about 10 per cent. of carbon monoxide was required to effect a similar reduction. Complete elimination of scaling could have been obtained only with percentages of carbon monoxide requiring too high a fuel ratio for economical operation.

The tests on the carbon steels were extended to include gas combustion atmospheres with small percentages of oxygen, *i.e.*, carrying an excess of air. These atmospheres were necessarily of complicated analysis and included various combinations of the gases carbon dioxide, carbon monoxide, hydrogen, methane, steam and, in certain cases, oxygen in addition to nitrogen. The scaling losses were found to vary with the composition of the atmosphere in a similar manner for all the carbon steels; as the gas/air ratio was increased to give percentages of carbon monoxide less than 2 per cent. a tendency for increased scaling losses was observed for all the steels, which became much more noticeable as a zero content of carbon monoxide was approached. With the appearance of free oxygen the scaling increased further but above 1 per cent. of oxygen the rate of increase in the scaling with increasing oxygen content fell off rather rapidly for three out of five steels. In general, the greatest increase in scaling

resulted from decreasing the gas/air ratio, so as to vary the combustion atmosphere from one containing 1 per cent. of carbon monoxide to one containing 1 per cent. of free oxygen; in some cases, this had the effect of doubling or tripling the scaling loss. Increases in the content of carbon monoxide beyond 2 per cent. resulted in a further gradual but slight decrease in scaling.

At 900° C., high carbon steels with 0·9 and 1·05 per cent. of carbon scaled least and medium carbon steels with 0·3 and 0·45 per cent. of carbon most, whilst 0·15 per cent. carbon steel gave an intermediate value.

In confirmation of the observations previously made by several investigators, the introduction of 0·1 to 0·2 per cent. of sulphur dioxide was found to cause an appreciable increase in the rate of scaling.

Upthegrove concludes with a general review of the factors that may affect the scaling and certain related phenomena. He points out that the so called " neutral " atmospheres contain steam and carbon dioxide, both of which are active oxidising agents at elevated temperatures. Although the use of sufficient excess fuel to give non-scaling conditions would be economically unsound, scaling can be appreciably reduced by the use of combustion atmospheres containing small percentages of carbon monoxide rather than of free oxygen. Unfortunately, however, the possibility of decarburisation must also be taken into consideration, since hydrogen and carbon monoxide are both powerful decarburising agents and the very conditions favourable for the reduction of scaling thus tend to promote decarburisation. It may, however, be concluded, from data given by Jominy on the maximum permissible heating time in various atmospheres at different temperatures, if decarburisation is to be avoided,[6] that at the lower temperatures it should be possible to utilise atmospheres carrying sufficient reducing agents to ensure low scaling losses without causing decarburisation during ordinary periods of heating; naturally, the permissible heating time without decarburisation decreases progressively with increasing temperature.

The conclusions reached by Murphy and Jominy[8] may be summarised thus :—

    (1) The scaling loss increases with :—

        (a) Increasing velocity of the gas stream up to a certain critical rate of flow, above which there is no further

increase; this critical rate, in Jominy's work, appeared to be less than 20 ft. per minute.

(b) Temperature, and becomes very great when the oxides are molten above 1370° C.

(c) Time, but at a decreasing rate.

(2) The scaling loss is proportional to the area, unless the surface/mass ratio is large.

(3) The scaling loss decreases with :—

(a) Decreasing partial pressure of the oxidising gas.

(b) Increasing carbon content in the steel above 0·5 per cent. At 1260° C. the scaling of carbon steels increased in the following order of carbon content, 0·9, 1·12, 0·15,0·50, and 0·30 per cent. carbon.

(4) The scale formed in steam, carbon dioxide, and mixtures of these with or without carbon monoxide or hydrogen at 1090 to 1370° C., consists largely of ferrous oxide, FeO, but magnetite Fe_3O_4 preponderates in that formed in air.

(5) Small amounts (0·1 to 0·2 per cent.) of sulphur dioxide increase the scaling loss and the sulphur content in the outer layers of the steel, oxysulphide inclusions being formed along the grain boundaries and within the grains; the deleterious effect of this gas increases with temperature and time but is less marked in a reducing than in an oxidising atmosphere. Sulphuretted hydrogen is far less harmful than sulphur dioxide.

(6) The scaling action or otherwise of products of combustion containing nitrogen, carbon dioxide and monoxide, steam and hydrogen in carbon and some more common alloy steels can be predicted with reasonable accuracy from the equilibrium ratios in the Fe : O : H. and Fe : C : O. systems which were redetermined by the authors, using a new method.

It may be added that the values of the scaling losses determined by Jominy and Murphy are in reasonable agreement with the later results of Upthegrove; thus in oxygen at 1093° C. the observed oxidation rates are equivalent to 0·0081 and 0·0093 in. per hour respectively. Jominy and Murphy, however, covered a higher temperature range from 1093° and 1316° C. and point out that at the highest temperatures, above 1260° C. in the case of oxygen and 1316° C. in that of air, the true oxidation rates are not observed since the steel becomes hotter than the furnace temperature. In this temperature

range, the rates of scaling in oxygen and steam were very similar and that in carbon dioxide somewhat greater than that in air; at the maximum temperature, about 1300° C., very similar oxidation-time curves were observed in all four media.

RESEARCHES OF SCHROEDER

W. Schroeder approached the problem from a rather more practical point of view. After unsuccessful attempts to conduct experiments in ordinary works reheating furnaces, he fitted up a small blacksmith's muffle in such a manner that it could be fired with gas, fuel oil or coke. In this muffle he conducted oxidation tests on over 2000 specimens of 0·34 per cent. carbon steel, each 2·4 in. long by 1 in. square, which were descaled by grinding prior to the tests. The blocks were placed on the hearth of the muffle and at the conclusion of the tests they were quenched in water and pickled electrolytically in an acid bath, so as to determine the loss in weight. The side of the block in contact with the hearth was disregarded in calculating the scaling loss per unit area but appears to have been oxidised to some extent owing to the unevenness of the hearth; this may partly account for the fairly large deviation, ranging up to 10 per cent., observed between duplicate results.

Schroeder's main conclusions may be summarised as follows :—

(1) By means of tests on steel objects of various shapes and sizes, oriented in different ways to the flame direction, he was able to show that the scaling per unit area was independent of these variables and, therefore, a constant under given experimental conditions, for a given temperature.

(2) Oxidation/time curves in a gas combustion atmosphere at 1000° C. with an air factor of 1·2 revealed a definite diminution in the rate of scaling with time, as shown in Table I.

The deduction of any general oxidation/time law from Schroeder's results is complicated by the fact that all experiments were started with a cold muffle and the times given include a heating up period of 30 minutes in all cases. We have, however, calculated the values of $W^2/(t-0·25)$, where W is the observed loss in weight and t the total heating time, thus diminishing the effective periods of exposure by 15 minutes; as will be seen from Table I, the observations can be approximately represented by a parabolic function.

TABLE I.—*Oxidation of 0.34 per cent. Carbon Steel in a Gas Combustion Atmosphere with an Air Factor of* 1·2, *at* 1000° C. (W. Schroeder)

Time (hrs.) (t)	Loss in Weight (mgrms./cm²)		$\dfrac{W^2}{100(t-0\cdot25)}$ (b)	Equivalent loss of metal (in.)
	W. observed	W. calculated(a)		
1	90	91	108	0·0045
2	145	139	120	0·0073
3	180	174	118	0·0090
4	215	204	123	0·0108
5	235	229	116	0·0118
6	250	252	109	0·0125
7	265	274	104	0·0133
8	270	293	94	0·0135

(a) $W^2 = 11,100\ (t-0\cdot25)$.　(b) Observed values of W.

(3) A more detailed series of tests, in the same gas combustion atmosphere, at temperatures from 900° to 1100° C. and with heating times from 30 to 120 minutes, inclusive of the 30 minutes heating up time, showed that the oxidation loss (W) over this period could be expressed by the linear formula, $W = x + bt$, where t is the heating time and a and b are constants. As already noted, there was some indication of a more or less linear variation of oxidation with time in the later stages of some of Upthegrove's experiments in air, and more particularly in carbon dioxide.

It is noteworthy that interpolation in Schroeder's results gives a value equivalent to a loss of metal of 0·0033 in. after one hour's heating at 930° C.; according to his graphs, this gas combustion atmosphere contained about 3·1 per cent. of free oxygen, 6·5 per cent. of carbon dioxide, and 17·4 per cent. of steam. In an atmosphere containing 3·6 per cent. of oxygen, 11·9 per cent. of carbon dioxide and an unstated amount of steam, Upthegrove reports a loss for 0·15 per cent. carbon steel after one hour's heating at this temperature, which is equivalent to 0·0027 in. of metal. Taking into consideration the entirely different experimental conditions, the two results agree reasonably well.

(4) The effect of differences in the velocity of the gas stream on the oxidation was also investigated but with negative results, since the working conditions of the muffle necessitated much higher velocities, from 80 to 1700 ft. per

minute, than those of Upthegrove. Within these limits the oxidation rate was independent of the gas velocity.

(5) The effect of variations in the air factor from 0·85 to 1·3 on the oxidation was investigated at temperatures of 900° (gas only) and 1000° and 1100° C., for all three fuels, gas, oil and coke. No distinction could be made in the scaling caused by each of the fuels when an air factor of one was used. The oxidation losses, for a standardised heating period of one hour, under these conditions were as follows :—

900° C. 0·035 g/cm. sq. equivalent to 0·0018 in. of metal.
1000° C. 0·06 ,, ,, 0·0030 ,, ,,
1100° C. 0·14 ,, ,, 0·0070 ,, ,,

Upthegrove's value for 0·3 per cent. carbon steel heated for one hour at 930° C. in a gas combustion atmosphere containing zero per cent. of carbon monoxide is equivalent to approximately 0·0023 in. of metal, whilst extrapolation in his results gives a value equivalent to 0·0042 in. of metal for 0·15 per cent. carbon steel exposed at 1040° C. under similar conditions. It will be seen that the two series of results are again in substantial agreement.

Schroeder points out, however, that, with an air factor of unity, the relative contents of steam and of carbon dioxide in the burnt gas varied considerably for the three fuels and it is therefore surprising that no difference in oxidation rate was observed. He adds that the experimental difficulties are greatest in the neighbourhood of the neutral point and that the possibility of inaccuracies in his curves between air factors of 0·95 and 1·05 cannot be excluded.

(6) The results bring out, in common with those of Upthegrove and other workers on the subject, the marked effect of small percentages of free oxygen on the oxidation. At 1100° C. an increase in the air factor from 1·0 to 1·1, which introduced about 1·6 per cent. of oxygen into the burnt gases, caused increases in the scaling of about 54, 37 and 14 per cent. when coal gas, oil and coke respectively were used for firing the muffle. On the other hand, also at 1100° C., a decrease in the air factor from 1·0 to 0·9 caused reductions in the scaling of 54 per cent. for coal gas, 31 per cent. for oil and 13 per cent. for coke. Schroeder attributes this marked difference in the relative effects of excess of air and deficiency of air respectively on the oxidation rate in the case of the three fuels to the fact that, when excess air is present, the

combustion products of coal gas and coke contain the highest and least proportions of steam respectively, whereas with a deficiency of air, the position is reversed and the coal gas combustion atmosphere contains most, and the coke combustion atmosphere least, hydrogen; hence steam is a more powerful oxidising agent than carbon dioxide and hydrogen a more powerful reducing agent than carbon monoxide.

(7) Analyses of the scale formed under different conditions of heating showed that, in general, the ratio of ferric oxide to ferrous oxide was greater when excess of air was present than when there was a deficiency of air, and also for oil firing than for gas. With both fuels this ratio decreased with increasing heating time.

The scales formed in atmospheres containing an excess of air were readily removed by quenching in water and left the surface of the metal smooth. On the other hand the scales formed with a deficiency of air could only be removed with difficulty and pickling was necessary to remove the last traces; moreover, the surface of the metal was roughened. Since this destruction of the surface was particularly marked in the case of coke firing and only slight in that of coal gas, Schroeder attributed it to the presence of carbon monoxide in the atmosphere. In view of Jominy's work it is not improbable that this roughness was associated with some surface decarburisation. Schroeder was able to eliminate this disadvantage by heating the specimens for 1 hour in an oxidising atmosphere at from 900° to 1000° C. and then for 1 hour at 1100° C. in a reducing atmosphere, after which the scale was easily removable and no damage of the surface was observed. He considers that this procedure might prove practicable and advantageous under works conditions. It will be noted that these differences in the behaviour of the various types of scale agree with Upthegrove's observation that scales formed in oxygen were readily removable but those formed in steam were only removed with difficulty.

RESEARCHES OF DICKENSON

In 1922, J. H. S. Dickenson published, as part of a more extensive investigation on the mechanical properties of steels at elevated temperatures, a note on the scaling of heated steels, which appears to constitute the first major quantitative communication on the subject. His tests were made on small

cylinders, 2 in. long by 0·5 in. diameter, machined from round bars and polished with emery; these cylinders were heated in air at temperatures from 575° to 1100° C., an electric muffle being used at temperatures up to 875° C. and a gas heated muffle above this temperature. Since Dickenson realised that the rate of oxidation slows down as the adhering scale increases in thickness, he adopted the plan, in order to maintain a uniform oxidation rate, of removing the specimens at regular intervals of about $5\frac{1}{2}$ hours, scraping off the scale and weighing them after each cooling before replacing them in the furnace, the process being continued for a total heating time of 100 hours.

It is clear that the experimental procedure does not enable true oxidation/time curves to be obtained but, since in the case of specimens of medium carbon steel tested by Dickenson, the oxidation varied directly as the total heating time, the values given by him for the rate of oxidation in grms. per sq. in. per hour may be used to calculate by simple proportion the total oxidation over the first heating period of $5\frac{1}{2}$ hours, from which the appropriate oxidation constant can be deduced, assuming a parabolic law (i.e., Dickenson's values should be multiplied by $\sqrt{5\cdot5}$). If Dickenson's results are treated in this way, they will be found to be in good agreement with those of subsequent investigators; for example, his value for the oxidation of 0·3 per cent. carbon steel at 1025° $+$ 25° C. is 0·0067 in. per hour as compared with Upthegrove's values of 0·0059 and 0·0049 in. per hour at 1010° and 1040° C. respectively.

It should also be noted that Dickenson was able to establish a simple relationship between the rate of oxidation and temperature, since he points out that " if the same data are plotted in terms of their logarithms, taking the logs of the absolute temperatures and the logs of the scaling rates as co-ordinates, the points still fall on to reasonably straight lines, in which case the relationship may be expressed as $R \propto T^n$, where R is the rate of oxidation and T is the temperature." As we shall see later, a similar empirical relationship was deduced at about the same time, both for iron and several other metals by Pilling and Bedworth.

RESEARCHES OF UTIDA AND SAITO

Utida and Saito report some experiments in which the increase in weight of coils of various thin wires on heating in

air at temperatures from 770° to 1110° C. was measured continuously by means of a special balance up to a period of two hours. Unfortunately, many important experimental details are not given, such as, for example, the shape and dimensions of the coils used and whether the wires were cleaned prior to the tests, but the data include curves for an iron wire of 99·7 per cent. purity and a piano wire of unstated analysis, which are of interest in the present connection. To interpret these results on the same basis as those of Upthegrove, it is necessary to convert the figures for the weight of oxygen taken up by the specimen to weight of iron attacked; since we shall have occasion to make a similar conversion in the case of the results of other investigators, we propose to describe the method of calculation in some detail.

If W is the weight of oxygen taken up by the specimen, *i.e.*, the increase in weight in grm., P the percentage of iron in the corrosion product and A the total surface of the specimen exposed to oxidation in cm², then the equivalent thickness of the oxidised metal layer in inches is given by :—

$$L = \frac{WP}{(100-P)\,A} \times \frac{0\cdot394}{7\cdot88} = \frac{0\cdot05\,WP}{A\,(100-P)}$$

taking the density of iron or steel as 7·88[*].

Since ferrous and ferric oxide contain 78 and 70 per cent. of iron respectively the oxide scale may be assumed to contain about 75 per cent. of iron and, as a matter of fact, all investigators who have made direct analyses of the scale, have found a value in close agreement with this figure. If therefore, we put P = 75, then—

$$L = \frac{0\cdot05\,W\,75}{25A} = 0\cdot15\,W/A$$

or L = 0·15 W inches, if A = 1 cm².

We may further note that true oxidation/time curves on a metal basis can only be derived from measurements of the weight increment, whether measured directly or deduced from the volume of oxygen absorbed, if the values of P and A remain constant throughout the experiment. We have already seen that, according to Schroeder, the ratio of ferric to ferrous oxide

* This value of the density is very slightly too high for carbon steels, but the error is negligible from the present point of view.

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decreases with increasing time of exposure, and, since the values of P/(100–P) for ferric and for ferrous oxide are 2·33 and 3·5 respectively, the possible effect of any progressive change in the average composition of the oxide layer should not be overlooked.

In the case of the experiments of Utida and Saito, the second condition, *i.e.*, that the area of the metal/scale interface should remain constant, was certainly not fulfilled, as they themselves appear to have realised, for they point out that the observed reduction in the rate of attack may not have been solely due to the protective effect of the oxide scale but also to the progressive reduction in the cross section of the metal core. We have calculated that, in the case of the data of Utida and Saito for iron wire at 1110° C. (diameter 0·55 mm.; total surface area 12·8 cm²) the observed weight increment after 60 minutes, 0·491 grm., is equivalent to 0·187 c.c. of metal, whereas the total initial volume of the specimen was 0·176 c.c. This apparently incongruous result—actually weight-increments up to 0·580 grm., after 120 minutes exposure were observed for this specimen—might be explained by some slight deviation of the value of P from 75, but it shows definitely that at the conclusion of the experiments the wires were almost completely oxidised and that the area of the metal/scale interface was thus practically reduced to nil.

We have dealt with this point at some length in view of the fact that other investigators have used coils of wire in their experiments and future investigators may wish to do so. For certain purposes the use of a wire specimen is advantageous, *e.g.* in the case of tests by the electrical resistance or the decrease in breaking load methods, but in such cases care should be taken to ensure that the decrease in metallic diameter resulting from oxidation is not excessive; on the whole, since the oxidation of metals is probably governed by a diffusion process, the use of specimens with a single plane surface exposed to the oxidising gas would appear to be the ideal experimental method in the case of loss or gain in weight determinations.

As already stated, the oxidation/time curves obtained by Utida and Saito show a marked diminution in the rate of oxidation with increasing time of exposure. Whilst for the reasons already given their data do not lend themselves to any rigorous discussion of the oxidation/time law, there can be no

doubt of the decrease in the rate of oxidation in the later stages of the experiments as compared with that observed in the first 15 minutes or so. Thus, we have converted their values for the weight increments at 890° and 1000° C. into the equivalent thickness of the oxidised metal layer (by calculating the volume of metal oxidised and hence the average reduction in the effective metallic diameter of the wire), with the results shown in Table II.

TABLE II.—*The Oxidation of* 99·7 *per cent. Iron Wire in Air at* 890° *and* 1000° C.[1] (Y. Utida and M. Saito)

Time (min). t	890° C.				1000° C.			
	Increase in weight (mgrm.)	W^2/t.	Thickness of metal oxidised L (in.)	$10^{10}L^2/t$	Increase in weight (mgrm.)	W^2/t.	Thickness of metal oxidised L (in.)	$10^{10}L^2/t$
5	31	192	0·00036	260	81	131	0·00099	1,960
10	46	212	0·00054	292	124	1,540	0·00158	2,500
30	91	276	0·00114	433	219	1,600	0·00297	2,940
60	127	269	0·00161	432	313	1,630	0·00467	3,630
90	153	260	0·00197	431	387	1,670	0·00646	4,640
120	176	258	0·00230	441	454	1,720	0·00950	7,520

[1] Diameter 0·055 cm.; original surface area of specimen 12·8 cm².

It will be seen that at 890° C. the oxidation, whether expressed in terms of the weight increment or of the computed decrease in metallic diameter, follows approximately a parabolic law after the initial stages of exposure; there is no evidence of this at 1000° C. On the whole, in comparing the results obtained by Utida and Saito with those of other investigators, we consider it best to base calculations on their results for 30 minutes' oxidation and to assume a parabolic variation of oxidation with time. Detailed values are given later in Table VI (see p. 59) but we may note here that at 1000° C. their figure for iron wire is equivalent to an oxidation of 0·0059 in. in two hours as compared with 0·0092 in. observed by Upthegrove.

RESEARCHES OF COBB, MARSON, ANGUS AND BLACKBURN.

In collaboration with C. B. Marson, H. T. Angus and W. H. Blackburn respectively, J. W. Cobb has published three papers

dealing with the influence of atmosphere on the scaling of mild steel. In the first of these, Marson and Cobb give the results of experiments in carbon dioxide/nitrogen atmospheres, dry air and carbon dioxide/steam atmospheres. If these are expressed in terms of inches of metal, the comparative results shown in Table III are obtained for reference to those of Upthegrove. .

TABLE III.—*The Scaling of Mild Steel in Various Atmospheres.* Thickness of Oxidised Metal Layer (in.) per 2 hours(*a*)

Atmosphere	C. B. Marson & J. W. Cobb			C. Upthegrove	
	Temperature ° C.	A	B	Temperature ° C.	C.
Carbon dioxide	900	0·00016	0·00020	900 (*b*)	0·00027
	1000	0·00065	0·00079	980	0·00071
	1150 (*c*)	0·00135	0·00165	1090	0·0049
Dry air	900	0·0030	0·0036	900 (*b*)	0·0026
	1000	0·0064	0·0078	1010	0·0083
79% nitrogen/ 21% steam	900	0·00071	0·00086	925	0·00146 (*d*)
Steam	1000 (*e*)	0·0041	0·0050	1010	0·0082

(*a*) The results of Marson and Cobb have been converted from a period of exposure of 3 hours, non-inclusive of an unstated heating-up period to the experimental temperature, to one of 2 hours by multiplying by 2/3 and $\sqrt{2/3}$ (columns A and B respectively) ; those of Upthegrove (column C) are observed values after 2 hours' exposure. No correction has been applied for the unknown heating-up period in the former case.
(*b*) Mean values for observations at 870° and 925° C.
(*c*) An isolated result ; temperature approximate.
(*d*) An interpolated value.
(*e*) According to Angus and Cobb.

On the whole, the agreement of the two series of results is to be considered satisfactory, especially as there is some doubt whether the rate of gas flow adopted by Cobb and his co-workers was sufficient to permit of oxidation proceeding at the maximum possible rate. The internal diameter of their furnace tube was 2 in.[7], so that their standard rate of flow, 2½—3 litres of gas per hour, is equivalent to a linear velocity of about 1 in. per minute, which is below the critical rates of flow reported by

Upthegrove of about 6 in. per minute for carbon dioxide at 750° C. and 5 ft. per minute for air and steam at 930° C.

Blackburn and Cobb consider it doubtful, however, whether the low rate of gas flow would affect the conclusions drawn from their experiments, which were chiefly concerned with the reduction of scaling by the addition of reducing gases, such as hydrogen and carbon monoxide, to the atmosphere. Under their experimental conditions (three hours' heating at 1000° C.), Angus and Cobb found that at least 58 per cent. of carbon monoxide was required in a mixture of this gas with carbon dioxide to prevent oxidation, whilst the presence of 50 per cent. of hydrogen in a mixture with steam had the same result. The rate of oxidation proved to be about 8 times greater in steam than in carbon dioxide. Consequently, the first effect of progressive additions of hydrogen to a carbon dioxide atmosphere was to increase the degree of oxidation, a maximum being observed with 26 per cent. of hydrogen, when the scaling loss was $3\frac{1}{2}$ times greater than in carbon dioxide alone; further additions of hydrogen reduced the oxidation, which ceased when about 57 per cent. had been added. In the case of carbon monoxide/steam mixtures, a large excess of about 80 per cent. of carbon monoxide was necessary to prevent oxidation.

Similar experiments were made by Blackburn and Cobb, who added various reducing gases to two types of atmosphere containing, in one case, 10 per cent. of carbon dioxide and 10 per cent. of steam and, in the other, 18 per cent. of carbon dioxide and 2 per cent. of steam, the balance in both cases being nitrogen, corresponding to the products of combustion of fuels rich and poor in hydrogen, respectively, such as a fuel oil and a dry high temperature coke. The results are shown in Table IV, the volume of reducing gas which it was found necessary to add to 100 volumes of the basis atmosphere to prevent scaling being given in each case. It may be added, as again illustrating the greater effect of steam on oxidation at high temperatures, as compared with carbon dioxide, that the observed rates of oxidation in atmospheres A (10 per cent. steam, 10 per cent. CO_2) and B (2 per cent. steam, 18 per cent. CO_2) were 0·0020 and 0·0011 in. respectively, after 3 hours' exposure at 1000°.

Blackburn and Cobb concluded that the amount of reducing agent necessary to prevent scaling or even to reduce it by half is much larger than could be used in ordinary practice. Even

TABLE IV.—*Additions of Reducing Gases Necessary to prevent Scaling in Synthetic Combustion Atmospheres at* 1000° C. (W. H. Blackburn and J. W. Cobb)

Composition of Atmosphere	Vols. of gas added to 100 vols of atmosphere	
	A. 10% CO_2 10% H_2O 80% N_2	B. 18% CO_2 2% H_2O 80% N_2
Reducing Gas		
Hydrogen	29.7	24.8
Carbon monoxide ..	95	65.6
Methane	20.8	—
Ethylene	7.1	—
Acetylene	8.1	—

in the case of hydrogen, the most efficient reducing agent on a thermal basis, the thermal expenditure amounts to 1·3 or 0·8 times the thermal value of the fuel used. They also made the interesting observation that free carbon, as such, in a smoky atmosphere had a negligible effect in preventing scaling, a clear atmosphere of the same composition being equally efficacious.

In a series of experiments in which small amounts of oxygen were added to the two synthetic combustion atmospheres, Blackburn and Cobb found that, whilst oxygen additions of one per cent. or more caused a marked increase in the oxidation, the addition of about a half per cent. had no such effect. We have already seen that the experimental difficulties are probably greatest in the immediate neighbourhood of zero oxygen concentration but it is also possible, as suggested by S. Tour,[13] that the composition of the " neutral " atmosphere may be affected by the temperature and the composition of the steel, and may not correspond to zero concentration of oxygen or of excess of reducing gas; for example, the curves of Upthegrove, particularly for certain alloy steels, seem to show that the steep upward slope on the oxidation gas composition curve occurs at different gas compositions for various types of steel.

A very interesting and encouraging comparison can be made between the results obtained by Blackburn and Cobb in these

synthetic combustion atmospheres, carrying small percentages of oxygen, and those of Schroeder, who, it will be remembered, worked on a semi-practical scale, using a small muffle. The results of the former workers, for tests over 3 hours at 1000° C., in atmospheres to which 3·8 per cent. of oxygen had been added, are equivalent to oxidation rates of 0·0024 and 0·0021 in. per hour in the case of the 10 : 10 and the 18 : 2 carbon dioxide/steam atmospheres, respectively, if oxidation is taken as proportional to the time or to 0·0042 and 0·0036 in. per hour, assuming a parabolic variation. Interpolation of Schroeder's results gives corresponding rates of 0·0047 and 0·0036 in. for oil and coke firing respectively with an air factor of 1·25, for which the analyses of the exit gases (3·8 per cent. O_2, 10·8 per cent. CO_2 and 9·2 per cent. H_2O in one case, and 3·8 per cent. O_2, 15·6 per cent. CO_2 and 1·2 per cent. H_2O in the other) were in reasonable approximation to the synthetic compositions used by Blackburn and Cobb.

Finally, Marson and Cobb report some interesting analyses of the scales produced in their experiments at 1000° C. The scale formed in air contained 24·3 per cent. of ferrous iron and 47·8 per cent. of ferric iron, corresponding to 31·3 per cent. and 68·3 per cent. of ferrous oxide and ferric oxide respectively, whilst that formed in a 20 : 80 steam/nitrogen mixture contained 65·4 per cent. of ferrous iron and 11·4 per cent. of ferric iron, that is, 84·1 per cent. of ferrous oxide and 16·2 per cent. of ferric oxide. This marked difference in the ratio of ferrous to ferric oxide in the scale formed under these different conditions is in agreement with the observation of Murphy and Jominy that the scale formed in steam at temperatures above 1090° C. consists essentially of ferrous oxide; as we shall see later, Heindlhofer and Larsen also confirm that the scales formed in steam and in carbon dioxide are principally FeO. Upthegrove reports, however, that a scale formed in air at 1010° C. contained 44 per cent. of ferrous iron.

RESEARCHES OF PILLING AND BEDWORTH

In 1923, N. B. Pilling and R. E. Bedworth reported a general investigation on the oxidation of metals at high temperatures and, in particular, gave the results of tests in which the weight-increments of coils of electrolytic and of ingot iron wire on heating at temperatures of from 600° to 1000° C. in air or oxygen were determined for periods of up to 24 hours. Full

experimental details are not given, and although the diameter of the wires used for the tests, which ranged from 0·08 to 0·23 cm., was greater than that used by Utida and Saito, the data show that an appreciable reduction in the diameter of the metal core occurred over the longest periods of exposure. Pilling and Bedworth state, however, that the mean surface area was reckoned for each specimen on the basis of the initial and final diameters.

Pilling and Bedworth concluded that the relationship between weight-increment and time was approximately parabolic, although the data adduced for most of their curves are far from conclusive and could scarcely be taken as sufficient to justify the existence of a parabolic law had this not been predicted by their brilliant theoretical reasoning and supported by analogous results obtained for other metals; they attribute the marked scatter of the results to the development of fissures in the scale and of locally oxidised areas. The oxidation of the ingot iron used in their experiment proceeded at a consistently greater rate and adhered more closely to a parabolic law than that of the electrolytic iron; in general, smoother oxide coatings resulted in the former case. There was some evidence, judging from the shape of the scale when cold, that a liberation of gas, puffing out the oxide, had occurred either during oxidation or on cooling.

In agreement with the contemporary observations of Dickenson, Pilling and Bedworth found that, as in the case of several other metals investigated by them, the relation between the " oxidation constant" (k), *i.e.* the square of the weight increment divided by the time of exposure, and the absolute temperature (T) was of the type $k = AT^n$ where A and n are constants. As will be seen from the general summary at the end of this review, the rates of oxidation in air and oxygen observed by them are in reasonable agreement with those of other workers; for example, their figure for ingot iron heated in air for 2 hours at 1000° C. is equivalent to 0·0096 in. of metal, whereas Upthegrove's value for mild steel at 1010° C. is 0·0083 in.

RESEARCHES OF HATFIELD.

Although the experiments described by W. H. Hatfield in 1927 were largely concerned with the resistance to oxidation of heat-resisting steels, parallel tests on mild steel and iron

were made as a basis of comparison, and the results obtained are therefore of interest in the present connection.

The majority of the experiments were conducted in a tube furnace on cylindrical specimens of about 1 cm. diameter previously polished to 00 emery. A standard time of exposure of 24 hours was adopted, after which the weight increment of the specimens was determined; the rate of gas flow was above 50 litres per hour in most cases.

The experiments may be divided into four groups :—

(1) The effect of slight modifications in the atmosphere was studied, small percentages of sulphur dioxide, carbon dioxide and steam, either singly or in combination, being added to the air passed over the specimens. The results obtained in the case of 0·17 per cent. carbon steel are given in Table V; we have added a column giving the equivalent thickness of the oxidised metal layer.

TABLE V.—*The Oxidation of 0·17 per cent Carbon Steel at 900° C. in Ordinary Air, Pure and with Various Additions* (W. H. Hatfield)

	After 24 hours exposure at 900° C.	
	Weight increment (mgrm/cm²)	Oxidised metal layer (in.)
Atmosphere.		
Pure air	55·2	0·0083
Atmosphere	57·2	0·0086
Pure air + 2% SO₂	65·2	0·0098
Atmosphere + 2% SO₂	65·8	0·0099
Atmosphere+5% SO₂+5% H₂O	152·4	0·0229
Atmosphere+5% CO₂+5% H₂O	100·4	4·0151
Pure air + 5% CO₂	76·9	0·0115
Pure air + 5% H₂O	74·2	0·0111

Hatfield concluded from these tests that the attack upon a typical mild carbon steel was profoundly increased by the presence of sulphur dioxide, carbon dioxide and steam in the atmosphere. He then proceeded to determine the oxidation rates in air of three steels at temperatures ranging from 100° to 1200° C. The data obtained for mild steel are included in Table VI (page 59). At the highest temperatures

Hatfield's results are in reasonable agreement with those of Upthegrove, bearing in mind the disparity in the periods of oxidation (24 and 2 hours respectively). On the other hand, Hatfield, in common with all other investigators, failed to observe the discontinuities in the oxidation/time curves later reported by Upthegrove.

(2) Experiments were also made in an unenclosed gas muffle and in a synthetic complex gas designed to represent products of combustion. The oxidation in the latter atmosphere, which contained 73 per cent. nitrogen, 5 per cent. oxygen, 12 per cent. carbon dioxide, 10 per cent. steam and 0·05 per cent. sulphur dioxide, after 24 hours' exposure at 900° C. was equivalent to 0·00171 in. of metal in the case of pure iron and to 0·0120 in. of metal in that of 0·17 per cent. carbon steel. The latter figure is 4·4 times the value deduced from Upthegrove's result (0·0027 in.) for a 0·15 per cent. carbon steel heated for 1 hour at 925° C. in a more or less comparable gas combustion atmosphere with 10·4 per cent. CO_2 and 5·6 per cent. O_2, and 3·5 times the value obtained by Schroeder (0·0035 in.) for a 0·34 per cent. carbon steel heated in a coal gas combustion atmosphere, which contained considerably more steam (about 16 per cent.). Disregarding the effect of differences in the composition both of the metal and of the atmosphere and assuming a parabolic oxidation/time law, Hatfield's result should be $\sqrt{24}$ or 4·9 times that of the other two investigators; the agreement is therefore reasonably good.

(3) In a further series of experiments, the effect of oxygen, steam, carbon dioxide and sulphur dioxide on various metals including iron, was investigated at 700°, 800°, 900° and 1000° C. The results for iron when heated in oxygen are in reasonable agreement with those of Upthegrove at temperatures of 900° and 1000° C., but are considerably higher than his results at 700° and 800° C. It is noteworthy that in sulphur dioxide at 900° and 1000° C. the iron sample was completely converted after 24 hours' exposure, and also that Hatfield failed to observe a marked difference in the respective oxidation rates in steam and in carbon dioxide.

(4) Hatfield's last series of tests was made on various industrial metals and alloys under the same experimental conditions as in the previous series. The rate of oxidation of a 0·17 per cent. carbon steel, included in these tests, was

consistently lower than that observed for iron, except at 1000° C. The observed rates of oxidation in oxygen are again in reasonably good agreement with those of Upthegrove, but are higher at the lower temperatures. Marked oxidation occurred in sulphur dioxide and at 1000° C. the specimen was completely converted. The rate of attack in steam was less than that in carbon dioxide at 700 and 800° C., and approximately two and a half times as great at 1000° C., whilst at 900° C. the two rates were equal. These observations do not agree with those of Upthegrove.

Hatfield pointed out that, since all steels contain carbon, sulphur and hydrogen, in varying, though in the latter cases small percentages, the products formed by the reaction of such elements with the gaseous atmosphere will be present at high temperatures, and this fact should be considered in any theoretical treatment of the results. He also concluded as a result of the research, that steam and sulphur dioxide in the gases materially increase the difficulties of withstanding their action; as we have already seen this latter statement has since been confirmed by the work of Cobb and his colleagues, and by that of Upthegrove and Schroeder.

Researches of Heindlhofer and Larsen

The paper of K. Heindlhofer and B. M. Larsen, which appeared in 1933, is more particularly concerned with the mechanism of oxidation, especially as affected by the constitution and properties of the scale layer. The authors also adduce experimental results, however, obtained by continuous weight determinations throughout the oxidation process. They agree with Murphy and Jominy that the effective oxidation temperature may be higher than that of the furnace, particularly when the metal is heated in oxygen. Their results are in qualitative agreement with those of other workers in that the scaling rates were observed to be higher in steam and less in carbon dioxide respectively than in air, although the quantitative agreement is poor; they consider that the greater rate of scaling in steam may be due to the greater porosity of the scale, and confirm that the scales formed in steam and in carbon dioxide, respectively, consist essentially of ferrous oxide.

Data given by these authors for the gain in weight of commercially pure iron specimens on heating in air for a

period of 100 minutes at temperatures from 700° to 1100° C., yield values for the oxidation rate in general agreement with those of other workers. Thus at 1000° C., Heindlhofer and Larsen's value is equivalent to 0·0064 in. or 0·0050 in. per hour (calculated according to a parabolic law, or by simple proportion) as compared with Upthegrove's value of 0·0059 in. per hour at 1010° C.

RESEARCHES OF PORTEVIN, PRÉTÉT AND JOLIVET

The most recent contribution to the literature of the subject is that of A. Portevin, E Prétét, and H. Jolivet, who preface the account of their experimental work with an admirable review and bibliography of the experimental methods available for the study of the oxidation of metals and alloys. Their own tests included experiments on electrolytic iron heated in oxygen for periods up to 8 hours at temperatures from 825° to 1000° C., in which the volume of oxygen that had combined with the metal was directly measured from time to time. The results obtained showed a decrease in the rate of oxidation with time, and were in accordance with a parabolic law over the longer periods; there was, however, a marked deviation from this law in the initial stages when the oxidation observed was less than that required by the parabolic relationship. A similiar deviation is apparent in the data of Utida and Saito reproduced in Table II (page 46).

The variation with temperature of the parameters of the parabolas fitting the later portions of the curves of Portevin and his colleagues is in good agreement with the previous observations of Pilling and Bedworth. It should, however, be noted that the French investigators observed a break in the curve obtained by plotting the logarithm of the parameter against the reciprocal of the absolute temperature; this occurred at about 900° C., and they attribute it to a variation in the velocity of the diffusion processes resulting from the transformation from alpha to gamma iron. It may also be significant that in the case of similar tests on ordinary mild steel they observed a marked and inexplicable scatter of the results between 800° and 900° C.

The rates of oxidation observed by Portevin, Prétét and Jolivet are in good agreement with those of other workers; thus after two hours' heating at 1000° C., 700 c.c. of oxygen

at N.T.P. were absorbed : since the surface area of the speci-
mens was 13·6 cm.², this corresponds to an oxidised metal
layer 0·0110 in. thick.   Upthegrove's value for mild steel
at 1010° C. is 0·0111 in.

SUMMARY AND CONCLUSIONS

We have dealt with each of the major researches on the
oxidation of ordinary iron and steel at some length in the
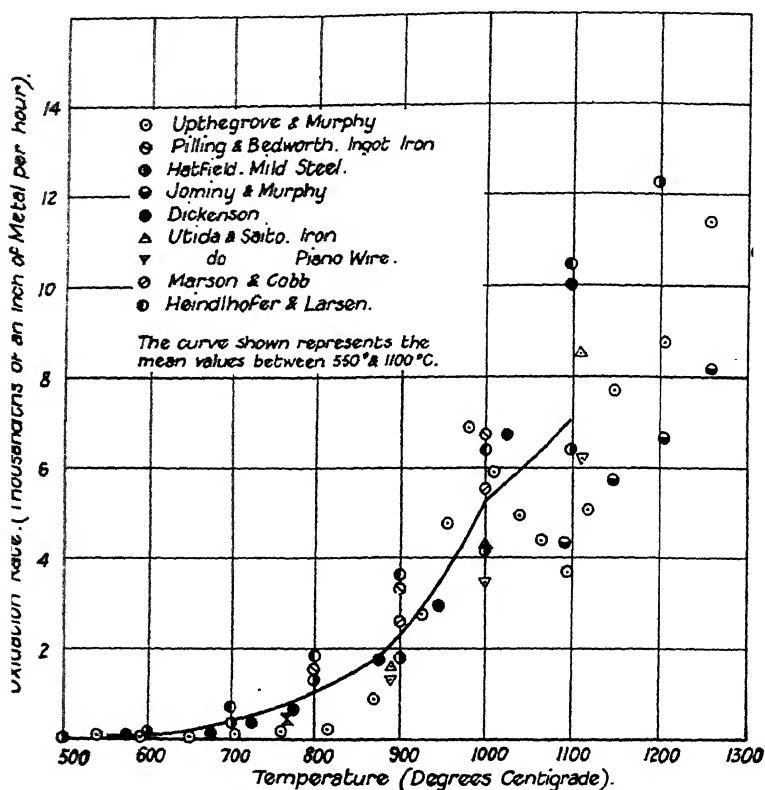
FIG. 1.—Experimental Values for the Oxidation of Iron and Mild Steel
in Air.

hope that we should thereby clarify the position as regards
the present state of knowledge of the subject, both for the
general reader, and as a basis for further experimental work
in this field.   It remains to summarise and correlate so far
as possible the results obtained by the various investigators.

(1) Although it would appear from the available evidence that the oxidation/time curves for iron and steel in air or oxygen are not truly parabolic, possibly as a result of disturbing factors such as the cracking and the complex composition
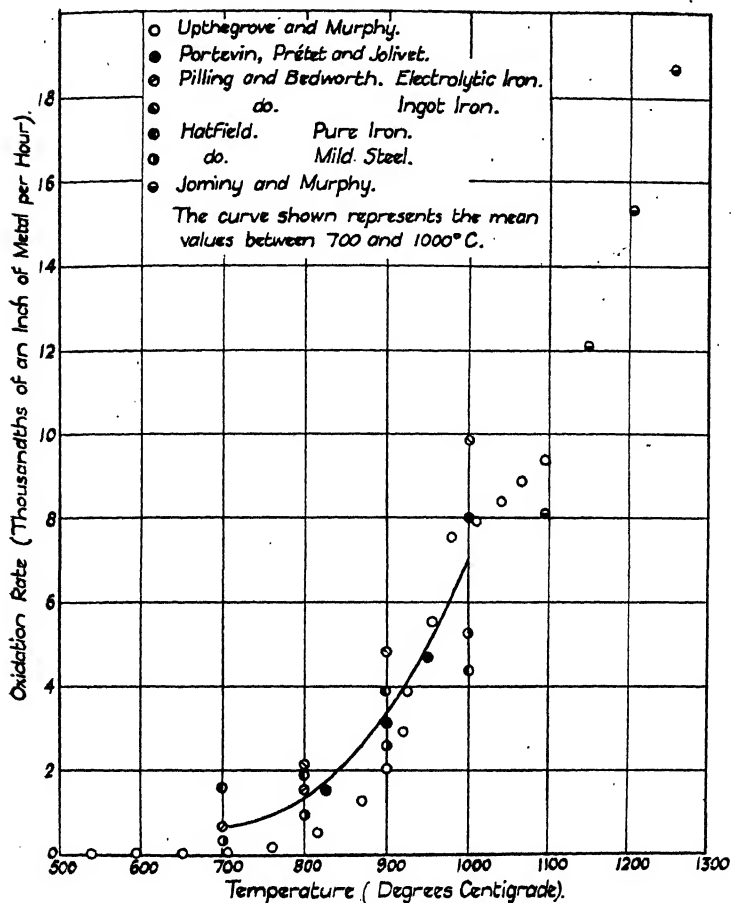
FIG. 2.—Experimental Values for the Oxidation of Iron and Mild Steel in Oxygen.

of the oxide scale, it is probable that for practical purposes a parabolic relationship may be assumed between oxidation and time. We have, therefore, reduced the values obtained by different investigators for the oxidation of iron and steel in air and oxygen to a common basis, assuming a parabolic law, and expressing the rate of oxidation in each case in terms

of the thickness of metal in thousandths of an inch, oxidised after one hour's exposure. The results so obtained, interpolated at intervals of 50° C. where necessary, are given in Tables VI and VII, and plotted in Figs. 1 and 2.
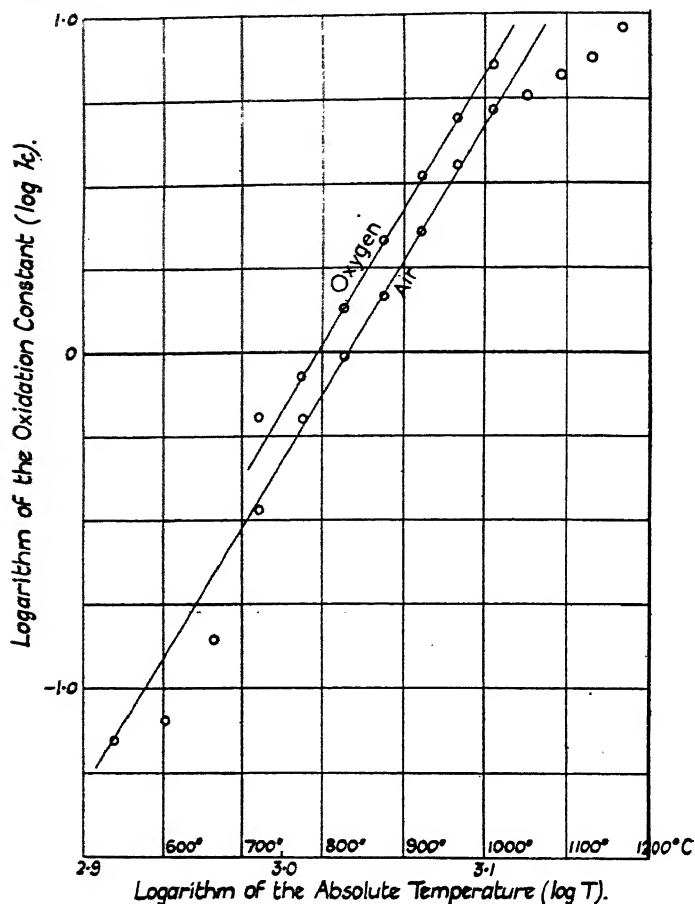
Fig. 3.—The Oxidation of Iron and Mild Steel in Air and Oxygen.

In view of the variety in the experimental methods and in the shape and composition of the specimens used by the different investigators, the agreement of the individual results is to be accounted satisfactory and, in our opinion, the mean values given in Tables VI and VII may be used with a reasonable degree of confidence to compute the probable extent of the

TABLE VI.—*Rate of Oxidation of Iron and Steel in Air at Various Temperatures.*[3]

Thousandths of an Inch per Hour.

Temperature °C.	Upthegrove 0.15% C. steel	Jominy & Murphy Steel	Hatfield 0.17% C. Steel	Utida & Saito — Iron	Utida & Saito — Piano wire	Heindlhofer & Larsen Commercially pure iron	Marson & Cobb 0.2% C. Steel	Dickenson 0.3% C. Steel	Pilling & Bedworth Ingot iron	Mean	Calculated Value (1)	Calculated Value (2)
550	0·05		0·08							0·07	0·07	0·042
600	0·05		0·14							0·08	0·13	0·092
650	0·05		0·25							0·14	0·22	0·18
700	0·08		0·37							0·34	0·37	0·34
750	0·09		0·87	0·59	0·61	0·68				0·65	0·60	0·59
800	0·15		1·38	1·04	0·94	1·14		0·05		0·99	0·96	0·99
850	0·50		1·56	1·76	1·48	1·80		0·12	1·55	1·47	1·50	1·56
900	1·66		1·75	2·84	2·33	2·54	2·55	0·23	2·30	2·27	2·30	2·39
950	4·20		2·95	4·20	3·42	3·60	4·03	0·50	3·32	3·62	3·47	3·52
1000	6·26		4·16	5·97	4·60	4·88	5·50	0·87	4·64	5·28	5·13	5·02
1050	4·64		5·00	8·05	5·96	6·39		1·40	6·79	6·07	7·51	6·99
1100	3·74	4·5	6·37			8·40		2·05		7·01	10·80	9·49
1150	7·65	5·7	8·80			10·45		3·10		7·38	15·33	12·62
1200	8·60	6·5	12·25					5·54		9·12	21·5	16·44
1250	10·8	7·8						7·80		9·3	21·5	16·44
1300		10·0						10·0			29·9	21·07

(1) $k = 1.664\,T^{2.83} \times 10^{-8}$.

(2) Log $k = 4.4944 - 4829/T$ where T is the absolute temperature.

(3) The values underlined thus 0·08 are interpolated; many of the results of Upthegrove have also been interpolated, as his experiments were made at Fahrenheit temperatures.

oxidation of iron and mild steel in a stream of air or oxygen at temperatures up to 1100° C.; the thickness of metal oxidised after a given period would be obtained by multiplying the figures given by the square root of the time in hours.
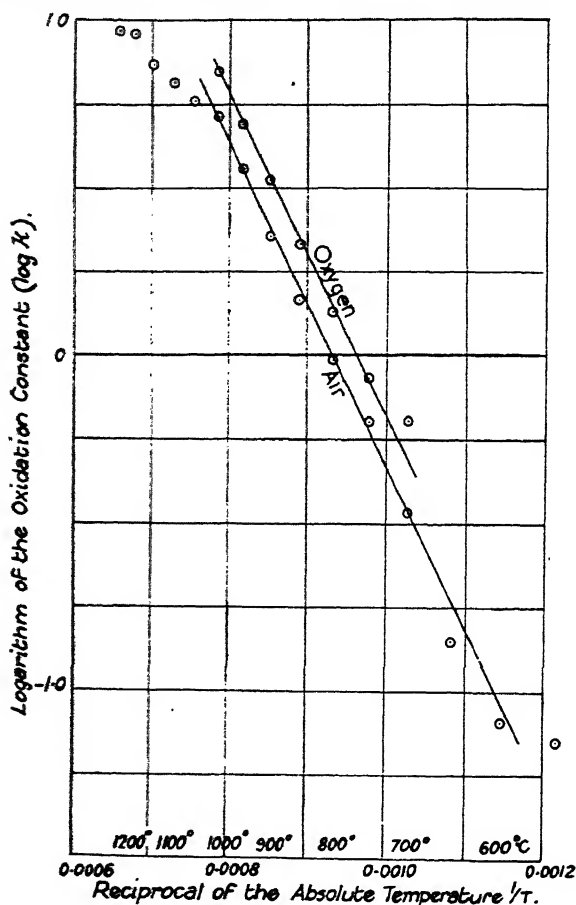
FIG. 4.—The Oxidation of Iron and Mild Steel in Air and Oxygen.

It is a matter of very great interest and possibly of fundamental importance that over a considerable range of temperature the mean values shown in Tables VI and VII adhere very closely to the empirical law of the type $k = AT^n$, deduced by Dickenson and by Pulling and Bedworth, connecting the oxidation constant with the absolute temperature T. Thus, at temperatures from 550° to 1000° C., the

TABLE VII.—Rate of Oxidation of Iron and Steel in Oxygen at Various Temperatures.[1]

Thousandths of an Inch per Hour

Temperature °C.	Upthegrove 0.15% C. Steel	Jominy & Murphy Steel	Portevin&c Electrolytic iron	Pilling & Bedworth Electrolytic iron	Pilling & Bedworth Ingot iron	Hatfield 99·92% Iron	Hatfield 0·17%C Steel	Mean	Calculated Value (2)	Calculated Value (3)
550	0·05									
600	0·05									
650	0·05									
700	0·07			0·62		1·56	0·32	0·64	0·51	0·48
750	0·16			0·98		1·69	0·58	0·85	0·84	0·84
800	0·39			1·50		1·82	0·91	1·34	1·34	1·40
850	0·92		1·93	2·40	2·09	2·82	1·58	2·13	2·09	2·22
900	2·02		3·09	3·82	3·13	3·81	2·55	3·34	3·20	3·38
950	5·00		4·65		4·77	4·08	3·78	4·91	4·83	4·98
1000	7·80		8·01		7·03	4·34	5·23	7·04	7·14	7·12
1050	8·60				9·84					
1100	9·46	8·6								
1150		12·1								
1200		15·0								
1250		18·1								

(1) The values underlined thus ·93 are interpolated; many of the results of Upthegrove have also been interpolated, as his experiments were made at Fahrenheit temperatures.

(2) $k = 2 \cdot 316 T^{9 \cdot 28} \times 10^{-30}$.

(3) $\text{Log } k = 4 \cdot 6461 - 4829/T$ where T is the absolute temperature.

relationship between the rate of oxidation in air and the absolute temperature is adequately represented by the equation :

$$k = 1 \cdot 664 \, T^{9 \cdot 82} \times 10^{-30}$$

and that in oxygen, between 700° and 1000° C., by the equation :

$$k = 2 \cdot 316 \, T^{9 \cdot 82} \times 10^{-30}$$

k being in thousandths of an inch per hour in both cases. The linear variation between log k and log T is clearly shown in Fig. 3.

Alternatively, as is clear from Fig. 4, the relationship between oxidation and temperature may be expressed as :—

$$\log k = 4 \cdot 4944 - 4829/T, \text{ for air, from } 550° \text{ to } 1000° \text{ C.}$$

or $\log k = 4 \cdot 6461 - 4829/T$, for oxygen, from 700° to 1000° C.

There is some theoretical basis for a relationship of the latter type.

(2) It has been definitely established that, at the high temperatures reached in the hot working of iron and steel, carbon dioxide, steam, and sulphur dioxide are very active scaling agents. The effect of each of these pure gases has not been so widely investigated as that of air or oxygen, and the data available are less concordant than those for the latter gases, as will be seen from Tables VIII and IX, in which the results of experiments at from 700° to 1000° C. in carbon dioxide and steam respectively, are summarised.

(3) There can also be no doubt that small amounts of sulphur gases, and particularly of sulphur dioxide, in the oxidising atmosphere produce a marked increase in the degree of oxidation. So far as pure sulphur dioxide is concerned, the results of Hatfield show that at temperatures below about 900° C. its effect is of the same order as that of carbon dioxide or steam; above this temperature, however, there is a most pronounced increase in the rate of attack. As regards the effect of traces of this gas, we are given to understand in a private communication from Professor Cobb that, since the publication of the earlier papers referred to in this review, further experiments have been made in which the addition of varying amounts of sulphur dioxide to the two types of synthetic combustion atmospheres used in his work was found to produce a definite increase in the amount of scale

formed. This increase was not, however, directly proportional to the amount of sulphur dioxide added; additions of up to 0.01 per cent. had a very marked effect, but at this point there was a discontinuity in the oxidation/sulphur dioxide

TABLE VIII.—*Rate of Oxidation of Iron and Steel in Carbon Dioxide at Various Temperatures*

Thousandths of an Inch per Hour. (a)

Temperature °C.	Upthegrove	Marson & Cobb	Hatfield.	
			Iron	Mild Steel
700	0·09	—	0·37	0·06
800	0·07	—	0·45	0·23
900	0·14	0·08	0·71	0·47
1000	0·59	0·32	1·10	0·58

TABLE IX.—*Rate of Oxidation of Iron and Steel in Steam at Various Temperatures.*

Thousandths of an Inch per Hour. (a)

Temperature ° C.	Upthegrove	Angus & Cobb	Hatfield	
			Iron	Mild Steel
700	0·12	—	0·39	0·02
800	0·65	—	0·53	0·14
900	1·75	—	0·36?	0·47
1000	3·82	2·05	1·11	1·44

(a) These figures have been deduced by simple proportion from observations made at periods of from 2 to 24 hours by the respective investigators since, according to Upthegrove's results the oxidation/time curves are approximately linear. Some of Upthegrove's results are interpolated values.

concentration curve, after which further additions of sulphur dioxide had a much smaller but still quite definite effect. Examination of the metal disclosed that up to the point of discontinuity, sulphur was not present in the metal or scale, but beyond that point it was present, although not

THE OXIDATION OF NON-FERROUS METALS

By J. S. Dunn, Ph.D. and F. J. Wilkins, Ph.D.

The pioneer work in the field of oxidation of non-ferrous metals was carried out by Pilling and Bedworth, as described in Dr. U. R. Evans's introductory section. They divided the metals into two classes—those which oxidised to give protective coatings, and those whose oxide was formed in such a manner as to offer no hindrance to further attack. In the latter class were placed magnesium and calcium, while Vernon has shown that at low temperatures zinc also oxidises linearly with time.

The experiments of Pilling and Bedworth present two curious features. First, the linear oxidation is linear only up to a point and then becomes practically instantaneous, and secondly, the temperature coefficient is abnormally low. The oxidation rate is only increased about sixfold for a rise in temperature of 200° C., while a reaction limited by chemical factors should increase between one million- and one hundred million-fold. These results do not appear to be consistent with a chemical limitation. They might be consistent with a thin film pseudomorphic with the underlying metal constantly breaking down to a granular film and constantly renewed. This point appears to be academic, but might be of importance. The inconsistency has stood unchallenged now for ten years, and further work on these linear oxidations would be well worth while.

The majority of the common metals are protected by the films formed as the result of oxidation, and oxidise according to the parabolic law—

$$W^2 = Kt.$$

In some cases considerable deviations from the parabolic law are observed, for the oxidation rate slows down very much more rapidly than would be expected from the earliest oxidation. This change is assumed to be associated with

necessarily in both. Further experiments are being made to confirm these important observations.

(4) The effect of various mixtures of gases, whether of synthetic compositions or corresponding to actual combustion atmospheres, involves so many variables that it does not lend itself to a general summary; we have already correlated the results obtained so far as possible when considering the contributions of the individual investigators. Two facts, however, emerge very clearly :—

(a) Small amounts of excess oxygen in a so-called "neutral" atmosphere have a marked effect in increasing oxidation.

(b) Oxidation can be reduced by the use of combustion atmospheres containing a reducing gas, such as result from incomplete combustion of the fuel; but the reduction in scaling so achieved is offset for practical purposes by the decreased thermal efficiency of the heating process. Any practical application of these facts would involve the balancing of these two opposing factors. In view of the experimental work of Cobb and his collaborators it is improbable that the complete prevention of scaling by this method would be commercially advantageous, leaving out of account any question of the decarburization that might result in the case of steel, but some advantage might accrue by its partial adoption in certain cases.

(5) It is clear that, although much work has already been done on the oxidation of iron and steel, the whole subject requires much more detailed and extensive study. Thus :

(a) The oxidation/temperature curves for iron and steel should be redetermined over a temperature range up to at least 1400° C., since it is not uncommon for temperatures well above 1300° C. to be reached in steel-heating furnaces, whilst in the case of wrought iron the temperature may almost equal the melting point of the material (c. 1500° C.). The existence of the maximum and minimum points in the curve for air and of the point of inflection in that for oxygen reported by Upthegrove, requires confirmation, as does also the discontinuity in the oxidation rate observed by Portevin, Prétet and Jolivet on passing from alpha to gamma iron. Further investigations on the exact relationship between oxidation and time in the various gases at constant temperatures are

also desirable. The behaviour of iron and steel in steam and carbon dioxide atmospheres particularly needs re-investigation, as the existing data are conflicting.

It should also be remembered that low rates of scaling may be of considerable practical importance in cases where the material is exposed to the oxidising medium for prolonged periods, particularly if subject to stress. Since most of the published data refer to oxidation at temperatures in the heat treatment and forging ranges, it is also desirable that further investigations should be made at the lower ranges of temperature, such as obtain for example, in boiler practice.

(b) The effect of composition on the degree of oxidation, even in the case of the plain carbon steels, is obscure and requires elucidation; thus, the effect of differences in the carbon content of steel and of variations in the amounts of companion elements such as manganese, phosphorus, sulphur and silicon present should be thoroughly explored, not only from the point of view of the scaling loss, but from that of the subsequent effects of oxidation on the behaviour of the fabricated material, whether descaled or not.

(c) Further experiments on oxidation in gas and other combustion atmospheres could usefully be made, and in particular the effect of small amounts of sulphur gases in such atmospheres should be fully examined.

It is almost unnecessary to refer to the practical and economic importance of the subject; thus, in this country alone the annual loss of iron and steel due to oxidation in reheating furnaces probably amounts to well over a million pounds sterling in value.

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The experiments of Pilling and Bedworth present two curious features. First, the linear oxidation is linear only up to a point and then becomes practically instantaneous, and secondly, the temperature coefficient is abnormally low. The oxidation rate is only increased about sixfold for a rise in temperature of 200° C., while a reaction limited by chemical factors should increase between one million- and one hundred million-fold. These results do not appear to be consistent with a chemical limitation. They might be consistent with a thin film pseudomorphic with the underlying metal constantly breaking down to a granular film and constantly renewed. This point appears to be academic, but might be of importance. The inconsistency has stood unchallenged now for ten years, and further work on these linear oxidations would be well worth while.

The majority of the common metals are protected by the films formed as the result of oxidation, and oxidise according to the parabolic law—

$$W^2 = Kt.$$

In some cases considerable deviations from the parabolic law are observed, for the oxidation rate slows down very much more rapidly than would be expected from the earliest oxidation. This change is assumed to be associated with

sintering or recrystallisation of the oxide film. In this case, even, the parabolic law should be obeyed in the sense that W^2 should give a straight line plotted against time over the longer time intervals. The straight line would not, of course, pass through the origin, but would cut the time axis in a negative value.

The following metals have been examined and their oxidation curves plotted :—

Copper .. Parabolic oxidation from 50° to 1050° C. [10, 13, 19, 20] in the massive state.

In the disperse or activated state shows sintering phenomena above about 200° C.,[3, 9] but at 183° [23] C. apparently oxidises parabolically.

Nickel .. Parabolic oxidation from 800–1100° C.[13].

Tungsten .. Parabolic oxidation [5].

Cobalt .. Parabolic oxidation.[7]

Aluminium ⎫ Both show a great decrease in oxidation[13]
Cadmium .. ⎬ after a period of hours, owing to oxide
⎭ " sintering."

Lead .. Parabolic oxidation.[13]

Chromium Departure from parabolic law through sintering.[7]

It is proposed to deal with these metals and their alloys *seriatim*, discussing points of theoretical interest as they arise.

<div align="center">COPPER</div>

This metal has been studied perhaps in greater detail than any other, both in its massive form in which it is usually encountered in commerce, and in its disperse or activated form.

Massive copper has been studied from temperatures of 50°C. up to the melting point. Methods of experiment include the very careful weighings by Vernon[19] by means of which it was possible to follow gravimetrically the oxidation of copper plates at temperatures down to 50° C.

Dunn [3] used the interference colours of the oxide films from 180–240° C. He and subsequent experimenters showed that whatever might be the pitfalls to be expected from theoretical considerations, the thickness of oxide films can be estimated in the case of copper with quite fair accuracy. Hudson, Bucknall, Herbert and Ball [10] found by weighing

experiments that up to 600° C. copper oxidises parabolically and quite regularly, although Pilling and Bedworth found oxidation to be erratic below about 800° C., and attributed variations to cracking of the oxide film. Pilling and Bedworth and Dunn found the parabolic law in operation right up to the melting point of copper. Feitknecht[8] thought he detected departures from the parabolic law during the earliest stages of film formation, and attributed these irregularities to grain growth in the copper oxide, but Wilkins[20] showed that the results fitted the equation—

$$x^2 = Kt + c$$

where x = amount of oxide formed at time t, and K and c are constants. Wilkins suggested that under the conditions of Feitknecht's experiments the copper was likely to suffer appreciable amounts of preliminary oxidation, and therefore, interpreting c as equal to x^2 when t was zero, proposed that the results satisfied the normal parabolic law. If this proposal is accepted, important conclusions follow, for, since Feitknecht showed that during oxidation extensive grain growth took place, we are driven to the view that diffusion of oxygen through the oxide film proceeds at the temperatures of these experiments, through the lattice itself and not along the grain boundaries.

The temperature effect is well represented up to 600° C. by the expression connecting reaction velocities with temperature, *i.e.*, oxidation rate $= Ae^{\frac{-Q}{RT}}$.

A and Q are constants and R and T have their usual significance.

If the customary plot of log reaction velocity against $\frac{1}{T}$ is made, two straight lines are obtained, merging into one another at about 600° C.

The oxidation of activated or disperse copper obtained by repeated low temperature oxidation and reduction of normal copper has been studied fairly intensively.

Palmer [11] first noted the accelerated oxidation of activated copper. Dunn [3] showed that with progressive activation the oxidation curve departed more and more from the simple parabolic relationship and exhibited " sintering " phenomena at temperatures of 200° C. and above. Constable [1] studied film formation on activated copper, and concluded, after elaborate spectrophotometric measurements, that the colours

of thin film were true interference colours. Constable assumed that the films were cupric oxide, but it is generally agreed that the oxide film is almost entirely cuprous oxide. Both Palmer and Dunn reported that the temperature coefficient of the oxidation rate was abnormal at about 200° C., being negative over a short interval. The oxidation of activated copper shows undoubted evidence of oxide film sintering above about 220° C. Wilkins states that it is definitely parabolic below 180° C.

The influence of the pressure of oxygen upon the rate of oxidation has been studied by Pilling and Bedworth for massive copper, and by Hinshelwood and Wilkins for both ordinary and activated copper.

The method employed by Hinshelwood [9] consisted in heating copper and oxygen together in a closed system and following the course of the reaction by the decrease in the oxygen pressure. He was unable to reach any satisfactory conclusions since most of his experiments were carried out at temperatures of about 300° C., where sintering of the oxide film is considerable.

Wilkins employed exactly the same method, but worked for the most part at much lower temperatures, i.e., 150–200° C. He was able to show that the rate of oxidation was dependent on the rate of four processes :—

(a) The rate at which oxygen strikes the oxygen/oxide interface.

(b) Rate of evaporation of oxygen from the oxide/oxygen interface into the interior of the oxide film.

(c) The diffusion of oxygen through the oxide.

(d) The reaction between oxygen and copper.

At high pressures the diffusion of oxygen through the oxide film is the controlling factor. As the pressure is reduced, a point is reached at which this ceases to be true. This pressure, called the limiting pressure, is the higher, the more active the copper surface, and is thought to be the pressure at which the oxide film is just saturated with adsorbed oxygen. Activation of a cuprous oxide surface will increase the rate of evaporation of oxygen into the oxide layer owing to the increased number of grain boundaries. In order to saturate an activated surface under these conditions, a higher gas pressure is needed than for an inactivated surface. By studying the initial stages of the oxidation of an already oxidised copper surface,

Wilkins was able to follow the building up of the adsorption layer at the oxide/oxygen interface, and was able to show that the more activated was the surface the longer was the time necessary to saturate the interface with gas.

The following is probably a fair summary of our knowledge of the oxidation of copper.

The rate of oxidation is the result of (1) the rate of saturation of the oxide/oxygen interface; (2) the rate of diffusion of oxygen through the oxide; (3) the rate of combination of metal and oxygen. Except under special circumstances the rate of diffusion is normally the limiting factor.

The measurements of Vernon from 50° C. are perfectly continuous with those of Pilling and Bedworth up to 1000° C., and give an excellent straight line plot of log $K/\frac{1}{T}$ up to 600° C. The measurements of Pilling and Bedworth from 1000° to 700° C. also give an excellent straight line, but the values of these authors for 500° and 600° C. fall upon neither of these lines. All these measurements were made in oxygen. If one combines the values of Hudson, Herbert, Bucknall and Ball with those of Pilling and Bedworth for oxidations in air, all the points fall upon two straight lines, intersecting at about 580° C., and the measurements of Dunn on copper zinc alloys containing 5 and 10 per cent. zinc also suggest that the relationship is linear down to about 600° C. An interesting point is that the energy of activation for the interval 600–1000° C. is almost exactly twice that of the interval 50–500° C., the deviation being probably within the experimental error. This is particularly significant in view of the quantum mechanism suggested and recalls a similar relation found for the electrical conductivity of sodium chloride.[12] There is a very general analogy between conductivity and diffusion as far as temperature coefficient is concerned, and this tends to weaken perhaps the suggestion of grain boundary diffusion below 600° C. and lattice diffusion above, but there is other and more conclusive evidence upon this point.

Activated copper is considered to be a rather disperse form of the metal, highly fissured, and containing many convolutions comparable in size with molecular diameters. When this is oxidised a highly disperse oxide film is formed with very many very small crystal units, and the oxygen first saturates and then passes down the discontinuities of the

film structure. Below about 180° C. the oxide remains as it began—disperse in structure—but at 200° C. sintering commences, the crystallites coalesce and the oxidation rate decreases for a while with rising temperature till a point is reached at which the temperature coefficient is normal once more. There is no sign of such a discontinuity in the oxidation of massive copper in the same temperature range.

If we postulate grain boundary diffusion below 180° C., and, further, that sintering becomes very noticeable at 200° C., it is very apparent that grain boundary diffusion will be insignificant in the temperature interval 300–600° C., and that the discontinuity in the temperature-oxidation curve at about 600° C. on massive copper is not due to a change from grain boundary to lattice diffusion. Now the plot of log oxidation rate against $\frac{1}{T}$ is a perfect straight line for massive copper from 50° C. to 550° C., so that there is no change in mechanism in this temperature range. This leads to the conclusion that grain boundary diffusion is insignificant in the oxidation of massive copper at all temperatures above 50° C. It is important only in the oxidation of activated copper at low temperatures.

The oxidation of copper and, indeed, of most metals, is considerably accelerated by gaseous substances containing chlorine—Hudson, Herbert, Ball and Bucknall.[10] The precise mechanism of this accelerated oxidation is not known, but it is likely to be associated with the intermediate formation of chlorides and oxychlorides which give rise to a loose-structured oxide film abnormally permeable to oxygen. There is a temperature of maximum oxidation when chlorine compounds are present, since the annealing of the loosely structured film is tending to limit the oxidation rate, and annealing and sintering increase exponentially with temperature in the same way as reaction velocity. Thus, it occurs that there is a temperature at which the temperature effect on reaction velocity is great but at which oxide sintering has hardly commenced. Reaction velocities are lower at lower temperatures because of the usual temperature effect on reactions, and lower at higher temperatures because the sintering of the oxide film then becomes considerable.

No other gaseous constituents appear to affect the oxida-

tion of copper to any great extent, although sulphur compounds exert a slight accelerating influence.

No metallic impurity has yet been shown to accelerate the attack of oxygen on copper, although certain metals have a marked protective effect.

NICKEL

Far less attention has been devoted to the oxidation of nickel. Oxidation is apparently normal, both with respect to time and temperature, the parabolic and exponential laws being followed with accuracy, but the range of experiment has been far less than with copper. The effect of pressure has not been studied at all. Experimenters have been Pilling and Bedworth[13] and Dunn[7].

A feature of the oxidation of nickel is the preferential oxidation at grain boundaries resulting in the oxide being pegged firmly into the metal. As a result the scale on nickel is tightly adherent and cannot be flaked off. It is not certain that this effect would be noticeable with an absolutely pure nickel.

Nickel is specially sensitive to the action of chlorine compounds in the neighbourhood of 800° C., the accelerating action falling off rapidly as the temperature is raised above this point. The accelerated attack with air containing 5 per cent. hydrogen chloride is 27 times greater than the ordinary attack at 800° C. It is only twice as great at 900° C., and practically equal to the normal oxidation rate at 1000° C.

At 850° C. the greater part of the accelerated attack occurred in the first half hour, the oxidation curve showing thereafter a decided tendency to flatten.

These observations are consistent with the hypothesis of the formation of a loose structured nickel oxide from an intermediate compound of nickel, oxygen and chlorine of higher molecular volume. As the temperature is raised this film sinters to a more compact and impervious form, and the rate of oxidation is diminished. The gradual sintering also accounts for the flattening of the oxidation curve at 850° C.

COBALT

The oxidation of a sample containing Co 98.39, Ni 0.81, Fe 0.45, was examined by Dunn.[7] Oxidation was parabolic, and the influence of temperature from 700–1000° C.

was normal, the oxidation rate being proportional to $e\frac{-Q}{RT}$. There appeared to be no intercrystalline attack.

CHROMIUM

A few observations at 1000° C. were made[7] on electro-lytic chromium, 99 per cent. Cr and chrome metal (98 per cent. Cr). The electrolytic chromium oxidised considerably faster than the chrome metal, and showed an oxidation curve flattening with time. The oxide was rather soft and powdery. The chrome metal approximated more to a parabolic curve with a more compact oxide.

TUNGSTEN

The oxidation of tungsten has been studied by Dunn[5] for temperatures between 700° and 1000° C. All oxidation curves were good parabolas. The oxide was mainly the yellow WO_3 with a thin layer of the blue oxide.

There is a curious anomaly between 850° and 900° C., the rate of oxidation diminishing with rising temperature in a similar manner to copper between about 200° and 240° C. This is not due to annealing or sintering, both of which progress with time, for at the intermediate temperatures the oxidation is still perfectly parabolic and the oxide is therefore obviously in a state of equilibrium. It is most likely that equilibria are established between two forms of WO_3 in this temperature range, one form predominating up to 850° C., and the other above 900° C., but further evidence, such as X-ray or electron diffraction patterns, would be most welcome.

ALLOYS

The oxidation of alloys is subject to considerable complication. Consider two metals in an alloy X & Y. The following cases are possible. (a) X & Y form a continuous series of solid solutions, and upon oxidation momentarily a solid solution of the two oxides is produced.

a_1 This solid solution is stable.

a_2 XO is reduced wholly or in part by Y in the underlying metal.

a_3 XO and YO are not mutually soluble and segregate.

a_4 XO and YO form a compound which may or may not be miscible with XO or YO in excess.

a_5 The sintering of XO is catalysed by small quantities of YO.

a_6 XO is volatile and escapes.

(b) X & Y are not mutually miscible in the solid phase, a similar series of interactions between the two oxides or the two metals and two oxides again is possible, and it is not difficult to imagine further complications for both case (a) and case (b).

The following cases have been studied :—

(1) Copper-nickel alloys by Pilling and Bedworth.[14]

They found that the copper rich alloys oxidised at rates similar to copper, while nickel rich alloys oxidised at rates similar to nickel, with a slight approach to mean oxidation rates with progressive additions of either metal. The alloys at each end of the series oxidised parabolically, but the alloys with 40, 50 and 60 per cent. nickel were found to be abnormal with abnormal temperature coefficients. The oxidation rates of these alloys approximated to nickel at lower and copper at higher temperatures. Oxidation curves were not parabolic, but conformed to the expression : $W^{\frac{3}{2}} = Kt$.

Pilling and Bedworth represented the effect of temperature by the empirical expression oxidation rate $\propto T^2$.

Their experimental method depended on the fall in conductivity of wires undergoing oxidation, and they claimed to have demonstrated that the Cu-Ni ratio of the oxide was identical with that of the underlying metal.

A few unpublished experiments by the present author indicate that the behaviour of Cu-Ni alloys is rather more complex than this. The alloy " Corronil " is approximately 70 Ni, 30 Cu, with some manganese. At and below 850° C., the normal parabolic law is obeyed—at least for about 4 hours, the duration of the test—but at 900° C. and above, after a short period of normal parabolic oxidation, the resistance of the oxide film decreases considerably with a rapid increase in the rate of oxidation. This increase soon dies away and oxidation shows signs of following another parabolic curve with a considerably bigger constant K.

According to these experiments also, the composition of the scale differed considerably from the original metal. The relative values of the heats of formation of Cu_2O and NiO suggest that some reaction at the oxide-metal interface is inevitable with subsequent variation in Cu/Ni ratio in the scale and metal.

(2) The oxidation of the zinc-copper series (the brasses) has been studied by Dunn[6]. The series falls into the category a_2, since with copper contents up to about 80 per cent., any copper in the oxide film is immediately reduced by zinc diffusing out from the underlying metal, and at temperatures 580-880°C. all alloys with copper below 80 per cent. oxidise at exactly the same rate and the scale is practically pure zinc oxide. In this range, the oxidation is approximately parabolic, but apparently the zinc oxide is becoming less permeable the whole time, and an empirical equation

$$W^{2 \cdot 375} = Kt$$

is a fair representation of the observed facts at 725° C. The relative permeabilities to oxygen after $0 \cdot 25$ and $10 \cdot 00$ hours oxidation were found to be $\cdot 445$ and $\cdot 287$. It was found that by heating an oxide film in oxygen-free nitrogen, the film rapidly became almost impermeable to oxygen. This experiment would bear repeating.

There are one or two puzzling facts about zinc oxide films formed on brass. If sintering is noticeable at 725° C., and apparently it is, one would expect it to be so rapid at 800 and 880° C. that a true parabolic oxidation would be encountered owing to practically instantaneous sintering; but at 800 and 880° C. the same type of oxidation curve is encountered as at 725° C. with a slow fall in permeability of the film still in evidence. It has been suggested that lateral or grain boundary diffusion is responsible for the passage of oxygen, and that the passage of oxygen tends to " peptise " the structure and prevent coalescence of the grain boundaries. If all oxygen is removed as in the nitrogen annealing experiments, rapid coalescence occurs and the paths for further oxidation are closed. Any fresh angle on these puzzling observations would be most welcome.

Returning to the series of Cu-Zn alloys, up to 80 per cent. copper the diffusion of zinc to the surface of the alloy is sufficient to keep pace with the rate of arrival of oxygen through the film. In the interval 80-90 per cent., the rate of zinc

diffusion falls so that this equality cannot be maintained, and an oxide progressively richer in copper is obtained, until with 90 per cent. Cu the oxide itself has 90 per cent. copper in its metallic content. This is associated with parabolic oxidation at a rate very little lower than that of pure copper, *i.e.*, 5 or 6 times greater than for Cu contents below 80 per cent.

The oxidation of this series is governed by the following mechanism :—

(1) Diffusion of oxygen through oxide.
(2) Oxidation of metal surface.
(3) Diffusion of zinc up to metal surface.
(4) Reduction of copper oxide by metallic zinc.
(5) Re-entry of copper into the metallic surface.

This mechanism breaks down when (3) is not rapid enough and a normal oxidation then occurs. It is probable that the nickel-chromium series behaves in a similar manner.

Small quantities of nickel (up to 1 per cent.) and arsenic (up to 0·2 per cent.) are without influence on the oxidation of 70/30 brass at 775° C. Nickel is reduced like copper and re-enters the metal. Arsenic is volatile, so neither are found in the oxide scale.

Small quantities of aluminium exert a profound influence on the oxidation rates, showing a progressive protection till at 1·9 per cent. aluminium the oxidation rate is reduced to one fortieth of its original value. There is no doubt that the aluminium reduces both zinc and copper oxide, and a film of very resistant alumina is responsible for the low oxidation rate.

Aluminium bronze with 6·5 per cent. Al, remainder copper, is very resistant to attack, the oxygen uptake per cm^2 in 2 hours being only 0·172 mg O_2. There is a tendency for the oxide film to flake off, however.

COPPER SILICON

Massive elemental silicon is practically unattacked at 1000°C. A few experiments have been carried out on the Cu-Si series of alloys. The following were examined.

0·9 per cent. Si.   3·25 per cent. Si.   4·58 per cent. Si.
At 725°C. the 0·9 per cent. Si alloy oxidises parabolically and slightly less than pure copper.

The other two alloys appear to follow parabolic curves with breaks, and the oxidation is rather irregular and difficult to repeat. Considerable reduction in the rate of oxidation

compared with copper is found with the two higher silicon contents.

At 827°C., the 3·25 and 4·58 per cent. alloys commence to oxidise slowly, but there is a sudden increase in oxidation rate and subsequently the alloys oxidise at practically the same rate as copper. This is not surprising since the scale is found to contain no silicon, but it is difficult to conceive how the silicon remains unoxidised. For a tentative mechanism, see the original paper, but here again a repetition and extension of the work is needed. The form of the oxidation curves recalls that of " Corronil " at 900° C. and above.

The Nickel-Chromium Series

The writer cannot claim to have dealt with the nickel-chromium alloys exhaustively, and further information is to be found in Section VI of the Review, but the following facts were ascertained :

At 1000°C., the alloys containing 5 and 10 per cent. chromium both oxidised parabolically and at a progressively faster rate than nickel. Fifteen per cent. chromium gives a sudden drop in the oxidation rate and a change to a sintering type of oxidation curve. From 15 to 40 per cent. the rate of oxidation decreases continuously, the following figures repre- senting oxygen uptake in the first two hours :—

Composition	100% Cr	100% Ni	5% Cr	10% Cr	15% Cr	20% Cr	30% Cr	40% Cr
Oxidation Rate	1·6	2·34	3·12	4·04	0·56 0·84	0·21	0·18	0·11

All figures mg O_2 per sq. cm.

In the case of the resistant alloys, the oxidation rate subsequent to the first two hours is very much smaller.

Pure Chromium gives a rather soft oxide film readily abraded, but the nickel chromium alloys form an adherent scale and there are indications of " pegging in " by grain boundary attack.

Comparing the oxidation of chromium with nickel-chromium alloys, there seems to be evidence for the nickel in the oxide film catalysing the sintering of the chromium oxide, but there is no conclusive published evidence of the nature of this effect.

Oxidation Rate Constants "K" for Non-ferrous Metals $K = \dfrac{W^2}{t} = grs/cm^2/hr.$

	50° C	100° C	200° C	300° C	400° C	500° C	600° C	650° C	700° C
Copper in O₂	2.5×10^{-15}	1.6×10^{-13}	4.1×10^{-11}	6.6×10^{-10}	1.64×10^{-8}	1.93×10^{-7}	1.13×10^{-6}		5.86×10^{-6}
in Air					0.72×10^{-8}	$.419\times10^{-7}$	$.318\times10^{-6}$		2.68×10^{-5}
Nickel								1.6×10^{-6}	5.8×10^{-7}
Electrolytic Grade A in O₂								6.7×10^{-7}	1.61×10^{-5}
Cobalt (in air)									
Tungsten									
Brass (in air) 95—5									
90—10									

	750° C	800° C	850° C	900° C	950° C	1000° C	1050° C	1100° C
Copper in O₂		3.14×10^{-5}		1.27×10^{-4}	2.68×10^{-4}	6.02×10^{-4}		
in Air		2.70×10^{-5}		1.10×10^{-4}	2.46×10^{-4}	4.60×10^{-4}		
Nickel		$.093\times10^{-6}$		0.76×10^{-6}		3.4×10^{-6} 6.8×10^{-6}		
Electrolytic Grade A in O₂			0.64×10^{-4}	1.9×10^{-4}	3.4×10^{-4}			
Cobalt (in air)		3.3×10^{-6} 16.6×10^{-6} 22.5	7.35×10^{-5}	2.2×10^{-5} 17.9×10^{-5} 13.4	4.7×10^{-5}	7.4×10^{-5}	2.17×10^{-4}	
Tungsten			40×10^{-5}		116×10^{-5}	461×10^{-5}		13.3×10^{-6}
Brass (in air) 95—5		2.8×10^{-5}						
90—10		1.69×10^{-5}						

Copper in oxygen—measurements of Vernon and Pilling and Bedworth.
     air —measurements of Hudson, Herbert, etc., Feitknecht, Pilling and Bedworth.
Nickel —Pilling and Bedworth.
Cobalt —Dunn.
Tungsten —Dunn.
Brasses —Dunn.

SUBSCALE FORMATION

C. S. Smith, in a discussion on Dunn's paper [6], has drawn attention to the formation of " subscale " layers in many copper alloys. Underneath the scale proper is a layer of metal perfectly normal in every other respect, but consisting of " practically pure copper with nothing but oxygen in solution and with small solid particles of the oxide of the alloying element disseminated throughout." The effect is due to the diffusion of oxygen into the alloy, resulting in the oxidation of the alloying element and its precipitation in the form of insoluble oxide, leaving a matrix of pure copper containing oxygen up to the limit of solubility.

Under the somewhat artificial condition of maintaining oxygen pressure at or just below the dissociation pressure of the lowest oxide, subscale formation follows the parabolic law (since it is essentially a diffusion phenomenon).

This subscale is likely to be of importance since it will be present in most descaled annealed alloys and may most seriously modify the subsequent behaviour of the metal with regard to corrosion, etc.

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SECTION V.

OXIDATION AND SCALING OF FERROUS METALS FROM THE INDUSTRIAL POINT OF VIEW

By S. A. Main, B.Sc., F.Inst.P.

The Effects of Heat Scaling

Oxidation and scaling, as applied in general to the effects of the surface attack suffered by iron and steel when exposed to high temperatures in industry, are rather loose terms.

So far as the present statement is concerned, it has, however, been found convenient to use these terms indiscriminately when referring to the general problem, whether as applying to actual oxidation or to other forms of chemical attack, and also in those cases where there is no actual detachment of the surface products, such as the word scaling seems to imply.

Heat scaling of ferrous metals operates in industry on an extended scale and in many ways, almost always unfavourably, bringing difficulties in both the manufacturing operations and in the use of iron and steel, and causing wasteful expenditure.

(a) *In the Manufacture of Steel and Iron.*—Nearly all wrought iron and steel in course of manufacture necessarily has to be heated either for forging or rolling or for heat treatments, much of it undergoing more than one heating. Practically the whole of the iron and steel production is thus subject to a " tax," which, if proportionately not large, amounts in the aggregate to a considerable sum, representing the value of the total amount of steel and iron scaled away in this manner. With a British production of 7 million tons for the year 1933, and assuming a loss of not more than 2 or 3 per cent., the direct loss of material would be some 140,000 to 210,000 tons.

Direct loss of metal is not, however, the prime consideration. Scale acts as a hindrance and causes additional expense in many ways. It litters shop floors and furnaces and has a corrosive effect on the refractories. During rolling and forging operations labour is spent in loosening and clearing scale.

Optical pyrometric observations are hampered, and the

quality of the steel, as well as the efficiency of the processes, cannot therefore be so good as they otherwise might be.

Underneath the scale the surface is decarburised, thus, in the case of machined articles, increasing the amount of material to be removed. Pits or an uneven surface which result owing to patches of scale impressed during rolling or forging, accentuate this factor.

In heat-treating furnaces, the scaling is usually less severe than in those required for rolling and forging, since heat-treatment temperatures are in general lower, but decarburisation results with similar consequences. In the case of sheets, scaling in heat-treatment can have a roughening effect which is very undesirable and expensive to rectify when the sheets are required to have a good finish. This is specially the case with non-corroding steels which have to be used in a polished and immaculate condition.

(b) *In the Use of Steel and Iron.*—The disadvantages of the heat scaling of ferrous metals do not end with their manufacturing processes. They interfere with many of their applications, most obviously—but not entirely—where these materials are used at temperatures at or above a red heat. Steel used with a " black " surface derived in its manufacture is reduced in its strength, especially against fatigue, by the decarburisation and uneven surface underlying the scale, and this has been proved to be a serious disability in the case of springs, laminated and helical. There is consequently a growing tendency to go to the added expense of preparing a ground surface.

Rolling scale has an important effect in promoting the corrosion of iron and steel, particularly in its most objectionable form, that is, pitting. Especially in the case of ship plates, and structural steel, the weathering-off of the scale, and with it the paint, necessitates more frequent paintings in the early periods of use. The descaling of ship plates by weathering before painting practised in some cases removes these difficulties. The provision of suitable arrangements for storage, however, causes expenditure in another way.

The rolling scale on transformer sheets at one time gave trouble both because of its looseness, and, with the unevenness of the underlying surface, its reduction of efficiency by decreasing the " space factor ". Nowadays at some extra expense the scale produced in the hot mill is pickled off, and the surface smoothed by cold rolling.

The disabilities accompanying the use of iron and steel at temperatures above a red heat, arising from loss of strength and wastage due to oxidation, have necessarily in the past had to be countenanced where no other material would serve the purpose so well. Such uses are many and include, for example, fire bars and grates, flues and dampers, pokers and rakes, burner nozzles, smiths' and foregemen's tools, ingot moulds, rabbles, protective sheaths for pyrometer couples, and valves of internal combustion engines. The introduction of several new types of " Heat Resisting " Alloys, mostly, though not all, ferrous, soon after the Great War, favourably influenced this situation to a marked degree. Greatly extending as they did the range of use of metallic materials, not only much freer from the bane of heat scaling but some of them also an improvement in those mechanical properties for which steel and iron are valued, especially in high temperature applications, they not only solved many of the old problems, but made practicable new and improved processes and operating methods. Progress in the mechanical operation of reheating furnaces, usually involving the exposure of iron and steel parts to the heated zone, was facilitated. The expansion in the range of heat resisting " steels " occurred opportunely at a time when the economic and the other benefits of the more intensive working of furnaces and of high temperature processes were beginning to be appreciated, and were ready for development. As a consequence, progress in these directions has been rapidly going ahead with gain in experience, and continues to do so.

Heat resisting steels, whilst representing a great advance in practice, do not, however, represent perfection. The justification for their use must rest on considerations of performance against cost, and there are many cases where their substitution for ordinary steel or iron would not be economically sound. On the other hand, the advancing requirements of the engineer provide conditions which in some cases fully tax the capabilities of the best heat resisting steels yet available. Increasing intensity of furnace operations is advancing the range of temperature to be legislated for, while specially severe conditions arise in other ways, as for example with sparking plugs and valves of engines using petrol doped with tetraethyl lead.

The adoption by chemical and metallurgical engineers of these new steels in furtherance of their own developments of high temperature—high pressure chemical processes, has

further widened the scope of the problem. Formerly it was mainly concerned with the effects of the fairly clean atmosphere in the open or inside electrically heated furnaces, or of the particular forms of contaminated atmosphere in fuel fired furnaces, with, in some cases, actual contact with the fuel bed. Nowadays attack by a large variety of chemicals, both liquid and gaseous, and of molten metals has to be considered.

Against the mostly detrimental effects of oxidation and heat scaling must, in fairness, be mentioned a few cases where they serve a useful purpose. Millscale, as a readily available form of iron oxide, has its uses, particularly in open hearth and other steel making furnaces, and in the malleable iron process. There is also the " blueing " of clock springs, screws and other fittings, both to give a presentable finish and to retard rusting. The growing use of non-rusting steels, however, tends to detract from this practice.

SCOPE FOR INVESTIGATION

(a) *In the Manufacture of Steel and Iron.*—So long as the more ordinary kinds of iron and steel retain their uses on the present enormous scale there is obviously ample scope for improvement directed to the avoidance of heat oxidation and scaling in their manufacture. Non-corroding steels of the highly alloyed kind are much less subject to the difficulty, but neither these nor heat resisting steels can be expected to do much to reduce the quantities of ordinary steel required. Even if their higher cost were not a deterrent, they do not possess many of the mechanical and other properties required of steel and iron in their more general uses. Rather they have extended the applications for which ferrous materials can be used.

Although the effects of any lesser modifications in composition have not been fully explored, it seems hardly likely that any beneficial influence on the scaling characteristics of ordinary steels and irons will be achieved by this means without at the same time upsetting their other properties.

In manufacturing operations this disability of steel and iron must therefore be accepted as something with which it is impossible to deal adequately by modifications in the products themselves. The remedy lies mainly therefore in attention to the conditions to which the material is subjected while heated.

In this direction much has already been accomplished. In the past excessive scaling has occurred specially in forge and

rolling mill furnaces, due to the temperature being too high and maintained for unnecessarily long periods. Pyrometric control has effected considerable improvement in this respect.

Fuel fired furnaces have been steadily improved in design, mainly under the urge for economy and efficiency of working, but concurrently attention has also been given to avoidance of oxidising conditions, as well as of high local heating of the charge due to direct impingement of flame. Old standing false ideas as to the reducing character of a rich flame have been disproved, and the oxidising action of the products of combustion, carbon dioxide, sulphur dioxide and steam, even in the presence of considerable proportions of combustible gas, is established by the work of Cobb and others. Water vapour, next to oxygen itself, was shown to be the most active oxidising agent. Sulphur is specially obnoxious and is actually more active in a reducing atmosphere where it exists as H_2S, or organic compounds, than in an oxidising atmosphere as SO_2 or occasionally the higher oxide. If possible, its harmful effects are best avoided altogether by a suitable choice of fuel, as for example town's gas in preference to oil, rather than by any attempt to control them. The use of instruments recording composition of the gases has, so far as they have been applied, had a specially beneficial influence.

Electrically heated furnaces have in their limited sphere eliminated oxidation by combustion products, though naturally not that by the atmospheric oxygen itself unless special provision is otherwise made.

Heating in sealed chambers, or close annealing, has long been practised, especially in the case of wire and sheets, and the introduction of an inert gas is among more recent improvements. For this purpose, in one type of furnace the flue gases, rendered harmless by controlled combustion with a minimum of free air and by the subsequent extraction of moisture, are utilised.

Much further betterment in the situation at large as regards oxidation and heat scaling of iron and steel in manufacture may be looked for as a result of the full exploitation of the improvements mentioned, and others which will no doubt evolve from the ingenuity and experience of furnace designers. A universal solution covering all types and sizes of furnace is hardly, however, to be looked for as yet. Improvements in plant at large proceed slowly, partly from conservatism opposed to the permeation of scientific methods into what is often

regarded as an essentially practical operation, but also from the necessity to proceed by experiment or from the lack of immediate capital necessary to modernise or replace old equipment.

Protection of heated steel and iron during its transference through the atmosphere would seem to be a matter for ingenuity. Except in the case of large billets or forgings or castings, where the time of exposure may be rather long, the oxidation in these circumstances is probably of minor importance as compared with what may happen in the furnace. The inducement therefore to devise means of preventing it is correspondingly less, especially in face of obvious complications involved in the case of steel and iron passing to and from the rolls or the forge. Protection during the transference of smaller articles, as for example for quenching, has proved feasible and is being applied in many cases.

Scientific research in the laboratory and in a practical way in the further study of combustion will no doubt continue to aid the furnace designer. The discovery of new actuating principles would not in these days cause much surprise, and the possibility of the discovery of a method of combustion based on some chemical combination other than oxidation, and at the same time innocuous against steel and iron, cannot altogether be disregarded, even if it can only be limited in application.

In the absence of means of preventing oxidation entirely, it is desirable for many purposes for the scale to be of an easily detachable nature. This is the case, as mentioned, with plates and rolled sections which have to be painted. A hard adhesive scale on forgings, rolled bars and castings is damaging to the tools in the first roughing cut. Blisters are also a bugbear; if where they are present the remainder of the scale is adhesive, a patchy surface results after a little handling. When the whole surface is descaled it is badly marked at the locations of the pits. Attention has been given to these points, looseness of scale and freedom from blisters, as affecting sheets, in a recent paper by R. Griffiths to the Iron and Steel Institute[1], and this work might well be followed up in a more general way.

Studies of the mechanism of scale formation, such as those made by Pfeil, Jenkin, Winterbottom and Lewis, are also likely to be of practical service under present circumstances, but their utility in this connection will be diminished in proportion as improved methods of heating are developed.

(b) *In the Use of Steel and Iron.*—The disadvantages of scale on steel and iron in their main uses, i.e. at normal or only moderate temperatures, will naturally be diminished according to the measure of success attained in manufacture in avoiding oxidation or in removal of the scale. Separate research therefore seems hardly to be called for in the present connection.

In the use of steel and iron at high temperatures, it was by the introduction of special alloys that the first great step was made, and most progress has since that time been brought about by their modification or by the introduction of new and improved compositions. From experience of alloys in other directions it seems probable that still better combinations remain to be discovered, if only in the shape of alloys better suited to particular working conditions.

The trial of new alloys in the laboratory in various media at high temperature, would therefore seem to be a profitable line of research. It should be borne in mind that industry will not receive the full benefits even of existing types of alloy for some time to come, since much time is necessary for their exploitation. From this point of view the degree of importance of heat scaling in the use of ferrous metals, as influencing the urge for laboratory research, can hardly be judged at present, though there is undoubtedly a call for improved alloys.

A detailed description, necessary as a starting point, of the relative merits of the different types of ferrous alloy at present employed, and the particular conditions for which each is found to be suited can hardly be attempted here and, reference should be made to the many published papers and articles, of which that by L. J. Stanbery[2] is one of the most comprehensive and recent. In general the improved resistance to scaling of heat-resisting steels is achieved by the incorporation in various proportions of one or more of the elements, chromium, nickel, aluminium, cobalt and silicon. These elements appear to act mainly by the readiness with which they form protective oxide films; tungsten is also added in some cases to increase the strength at elevated temperatures. Of the large variety of heat-resisting steels now available, the most important are those of the iron-chromium, nickel-chromium-iron, iron-chromium-aluminium and iron-aluminium types. The amount of the alloying element may be considerable, as much as 30 per cent. of chromium being used in one well-known representative of the first mentioned, i.e. iron-chromium type, while the

range of iron-chromium-nickel alloys contains up to about 30 per cent of nickel. To these basic alloys, silicon, cobalt and tungsten are also added, usually in lesser proportions, to provide improved resistance to oxidation, either generally or to meet special conditions, or to increase the strength.

The iron-nickel-chromium alloys find the widest use because they combine resistance to oxidation and high temperature strength with considerable toughness. The iron-chromium alloys resist oxidation actually better, but are not so tough and tend to become more brittle in use; where resistance against sulphurous atmospheres is concerned, the plain iron-chromium alloys are again superior to those containing nickel, and further improvement both in this respect and against oxidation has been obtained by the addition of aluminium, which, however, makes for brittleness. The iron-chromium-aluminium alloys in fact so far provide the best materials available for applications involving particularly high temperatures, and have for example, extended the range of successful operation of electrical resistance heaters· to 1250—1300° C.

Mention should be made of the heat-resisting cast irons, that is, alloys with a cast-iron base to which special elements such as silicon, chromium or nickel and chromium, and aluminium are added. Just as in industry in general, there are uses for which the more ordinary cast irons are preferable to steel, so for similar reasons, there appears to be a limited field for heat resisting cast irons—more specially as an improvement in those cases hitherto served by ordinary cast iron such as grate bars.

The alloying elements used in the ferrous alloys are, it should be observed, much the same as those constituting the non-ferrous heat-resisting alloys. The most important of these non-ferrous alloys are based on combinations of nickel and chromium, with additions in some cases of manganese, silicon, aluminium, molybdenum or tungsten. Many of these, however, also contain iron in considerable proportion, and the two types therefore, ferrous and non-ferrous, tend to merge into each other. No hard and fast distinction can consequently be drawn among these particular alloys, for the purpose of classification as ferrous or non-ferrous. For the purpose of the present statement, only those alloys in which iron forms 50 per cent. or more of the whole are considered as being included in the terms " ferrous " or " heat-resisting steel."

The choice of new compositions for study as being likely to improve on the alloys now used presents much difficulty, both because the properties of new alloys remain as full of surprises and in most cases as incapable as ever of prediction, and also because of present limitations in the knowledge of the mechanism and chemistry of scaling. While the former must depend on general progress in the science of metallurgy, study of the latter can again in this connection be encouraged with advantage, especially as regards the individual roles played by the alloying elements. Many useful researches have already been carried out, among the more recent being those by Houdremont and Piwowarsky reported to the 3rd Congress of Industrial Heating, held in 1933, but there is room for much further work. Meanwhile, the researches have given indications likely to be of practical use. They have indicated for example, that carbides of chromium which may exist in grain boundaries, and which tend to increase in amount with long exposure at critical ranges of temperature, assist intergranular attack by oxidation and by sulphur. As a practical outcome the desirability of manufacturing methods which produce small grain structures, and control carbide precipitation is indicated. The development of methods of evaluating scaling properties on lines more scientific than those which exist at present, is also a necessity for further progress.

In the applications of heat resisting steels in the chemical industry, while individual study of the nature of the attack under the great variety of chemical compounds, their mixtures and reaction products, as well as of working conditions of temperature and pressure, must eventually prove of considerable service, the more direct method of selection of alloys according to their proved performance under practical conditions is necessary if progress is to be sufficiently rapid.

Improvements effected in the working atmosphere of fuel fired furnaces directed to avoiding scaling of the heated steel, will naturally react beneficially also on heat resisting alloys used in their construction. Elimination of sulphur, for example, by removing a disability of the nickel bearing alloys, widens the choice and makes possible a more suitable selection for the duty to be performed.

It is important to remember that in only a limited number of applications are non-scaling properties all-important, and that usually ferrous alloys are required to be rigid at high

temperatures, to sustain applied stresses or at least their own weight. They must also be tough to withstand rough usage. Workability, by which is meant capability of being prepared by forging, rolling, machining and welding, into the many forms required in industry, is also an important factor in the general utility of heat resisting alloys. In particular applications, some special property may have to be linked with the non-scaling characteristic, as for example a suitable coefficient of expansion in the case of valves of internal combustion engines.

Alloys of an intrinsically non-scaling character are likely to be of most use. Except in a few cases scale is likely to be knocked off or a thin oxide film damaged in the normal course of use. Materials which rely on their protective influence against further scaling are therefore liable to failure. In some applications, e.g., furnace skids and slicing links passing through the fuel bed and along the side walls of boiler furnaces, severe abrasion is part of the normal action to which they are subjected. The development of a scale even of the most tenacious kind in such circumstances, is of little advantage. These facts naturally have a bearing also on the use of protective coatings of aluminium and other metals. Where the coating is destroyed locally, experience shows that the consequent attack undermines the surrounding areas. Diffusion of the metal of the coating into the underlying steel incidentally also puts an upper limit to the temperatures for which this method can be employed.

Another cause of the flaking-off of scale is repeated heating and cooling, due to differential expansion and contraction between the scale and the underlying metal. This can occur even where the material is sheltered from mechanical damage, as in the case of electrical resistance heaters.

There is, however, a limited number of applications, including specially the supports used for the ware in enamelling and pottery firing furnaces, where a tenacious scale is desirable. Detached scale however slight is liable to blemish the surface of the ware. A readily fusible scale is equally objectionable. Complete absence of scale is of course the ideal, but is not yet achieved. Although the problem has already been met with a fair degree of success by alloys now in use, improvement is possible, and would be of benefit in the event of similar requirements being necessary at still higher temperatures in the natural course of progress. Equalisation of the expansion

characteristics of the scale and the alloy itself is, as mentioned, one of the factors for attention.

Among individual points of a practical nature suitable for research is the behaviour of castings as compared with forged or rolled material. No material difference in general scaling properties is usually found between these different types, so long as the chemical composition is the same, but castings are liable in some cases to a pitting attack. Since these pits extend and deepen, they sometimes perforate the castings, which therefore in such cases have a shorter life than much thinner rolled sheet material. The cases noted have been with steel containing 20 per cent. of chromium and 7 per cent. of nickel, and the pits occur in apparently sound castings, that is, they do not originate from visible defects.

A further peculiar feature experienced in the behaviour of heat resisting steels is the manner in which in some cases the non-scaling properties break down after a period of exposure. The cases noted have all been concerned with components where in the course of use the scale is continuously, or at intervals, being detached by abrasion. Forged material with a machined surface, as well as castings, shows this peculiarity, which cannot therefore be due to the removal, by scaling and abrasion, of a specially protective skin acquired in manufacture. It has been reproduced in carefully observed tests made on laboratory specimens in various types of oil, gas, and coal fired industrial furnaces. The specimens were taken from the furnace at intervals, and their loose scale removed by brushing and washing with hard soap.

Very few materials did not show this breakdown, although in some cases it did not occur until after 1900 hours of exposure. With a fresh surface prepared by regrinding, the normal characteristics are completely restored, though again suffering breakdown with continuance of the exposure.

In preparing this statement the author has drawn to some extent on the work and records of the Hadfield Research Laboratory, and he is indebted to Sir Robert Hadfield, F.R.S.. and Mr. W. J. Dawson, Metallurgical Director, for permission to make use of the information in question.

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SECTION VI

PRACTICAL ASPECTS OF THE OXIDATION AND SCALING OF NON-FERROUS ALLOYS

By L. B. Pfeil, D.Sc.

Apart from the precious metals, only a few non-ferrous metals and alloys possess a melting point sufficiently high to make their use possible as heat-resisting alloys. In addition to a high melting point heat-resisting alloys must possess a number of other properties including resistance to oxidation, resistance to corrosion at high temperatures by sulphur, chlorine and other compounds, resistance to distortion and good mechanical properties generally.

Copper-base and nickel-base alloys alone have any important commercial value as heat-resisting alloys. Copper offers a considerable measure of resistance to oxidation at temperatures up to about 500° C. and a large tonnage of this metal, with or without alloy additions, is used in applications where the temperature of the metal is not likely much to exceed 350° C. and where the mechanical properties of copper and its high thermal conductivity are specially valuable.

Nickel offers a high resistance to oxidation even at temperatures in excess of 1000° C. and was at one time in considerable demand for heat-resisting applications. The discovery of the remarkable heat-resisting properties of the nickel-chromium alloys, however, resulted in the displacement of pure nickel from many sections of the heat-resisting field.

Chromium does not form useful alloys with copper, except in the presence of a third element, such as will increase the solubility of copper for chromium. The improving effect of chromium on the heat-resisting properties of nickel is, however, to some extent paralleled by the effect of aluminium on copper, but although the copper-aluminium alloys offer a high resistance to oxidation, their usefulness is restricted by a relatively low melting point.

Apart from the nickel-chromium alloys and certain copper

alloys, commercial interest in the scaling characteristics of non-ferrous metals and alloys lies largely in methods of reducing or avoiding scaling during fabrication, and in methods of removing such scale as is formed during reheating, hot-working and annealing processes. During recent years much attention has been devoted to the development of bright annealing methods.

Although a large amount of information is possessed by the manufacturers and users of non-ferrous alloys regarding the scaling characteristics of the materials with which they deal, published information of a practical character is scarce. In the notes which follow, therefore, it is possible only in a few cases to give references to original publications.

NICKEL-CHROMIUM HEAT-RESISTING ALLOYS

The nickel-chromium alloys offer a high resistance to oxidation, and have good mechanical properties, both at ordinary and at elevated temperatures[12, 19]. These alloys possess electrical properties rendering them suitable for electrical heating apparatus and the greater proportion of the alloys made is converted into wire or strip for this application. The alloys are also used for furnace and other parts where electrical properties are unimportant. The most commonly used alloy contains 80 per cent. nickel and 20 per cent. chromium. It has been stated that at the 10 per cent. chromium level resistance to creep is at a maximum in binary alloys[3]. Oxidation resistance increases with increasing chromium content, but as the chromium is raised over 20 per cent. mechanical working becomes increasingly difficult, consequently the 80/20 nickel-chromium alloy has become a standard product which offers a specially serviceable combination of properties.

Nickel-chromium alloys containing from 10 to 40 per cent. chromium have found some applications, but where conditions are not sufficiently severe to merit the use of the 80/20 alloy it is most common to make use of a ternary nickel-chromium-iron alloy. These alloys are commercially available over the whole range of nickel contents from about 80 to 10 per cent., but the most important of the ternary alloys which can be placed in the non-ferrous category contains about 65 per cent. nickel, 15 per cent. chromium and 20 per cent. iron. This material is much used in electrical heating devices where

temperatures not much in excess of 850° C. are involved, but over the range 850° C. to 1100° C. the iron-free 80/20 nickel-chromium alloy is preferred.

Nickel-chromium base alloys are made containing additional elements, amongst which the more important are manganese, silicon, aluminium, molybdenum, and tungsten. A fairly complete list of the alloys available commercially was given by Herrmann[12].

The nickel-chromium and nickel-chromium-iron alloys are mainly used for three types of service (1) as castings, for moulds, boxes, etc; (2) as rod or sheet. for constructional purposes, furnace parts, etc.; (3) as wire, tape or strip for resistors in electrical heating apparatus. Broadly speaking, the nickel-chromium-iron alloys are mainly used for the first two types of service, while the binary nickel-chromium alloys are more particularly employed for resistors.

One of the principal difficulties encountered in researches on the nickel-chromium electrical-resistance alloys has been the devising of suitable methods for testing. Methods have been described by Smithells and his collaborators[22, 23], by Hessenbruch and Rohn[13], and by Bash and Harsch[1] and others. Many of the makers and users of these alloys employ laboratory testing equipment, but the general opinion seems to be that it is only by actual service tests that completely reliable information can be obtained. Most of the laboratory test methods involve the use of temperatures considerably in excess of those normally encountered in service, and the results of such tests are liable to be misleading, since it is known that the relative merits of different materials may vary according to the test temperature employed.

A number of researches making use principally of accelerated laboratory tests have dealt with the effects of additional elements and of impurities on the characteristics of nickel-chromium heat-resisting alloys [13, 22, 23]. Several elements, notably silicon, aluminium and molybdenum, have been shown to increase the life of nickel-chromium electrical-resistance elements, although there is evidence indicating that specially valuable properties are possessed by the 80/20 nickel-chromium alloy when the purity is high.

The properties required in electrical resistors are more complex than those required in heat-resisting alloys for most other types of service. Failure resulting from oxidation at

the normal working temperatures is seldom encountered in electrical resistors, and premature failure is generally due to local overheating, resulting from distortion produced by creep or careless handling. The popularity of nickel-chromium alloys is probably to be attributed more to a general reliability as a consequence of good mechanical properties and freedom from brittleness than to inherent oxidation resistance. Many of the modified nickel-chromium resistors, which, owing to the presence of additional elements, possess an improved resistance to scaling, possess inferior physical properties in other directions and, for this reason, have failed to find an extended market.

An important feature in connection with heat-resisting alloys generally is the quality of the refractory materials with which they come in contact. The protective scale which forms on chromium-containing alloys is liable to be destroyed by alkalies, and in the case of metallic resistors the presence of alkalies in the refractory materials is of special importance because of the possibility of concentration of the alkalies at the terminals by electrolytic action. This concentration is specially liable to develop where elements are worked on D.C. circuits and in bad cases the formation of alkaline chromates may lead to objectionable staining of the refractories and even the destruction of the element.

In non-electrical heat-resisting applications corrosion by sulphur compounds, or chlorine compounds in the furnace gases, is frequently at least as important as oxidation [25]. For this reason the nickel-chromium and nickel-chromium-iron alloys are commonly modified by additions of elements such as silicon, aluminium, and tungsten, while in cast products carbon is a common constituent, partly to increase the ease with which good castings can be obtained and partly with a view to improving strength at elevated temperatures.

The conditions which prevail in furnaces vary so markedly that a very large number of different alloys are employed; where oxidation resistance is of special importance the materials most commonly used approximate to binary nickel-chromium alloys, but where resistance to corrosion by sulphurous and other gases is of the greatest importance the materials generally employed are complex nickel-chromium-iron alloys commonly containing silicon and tungsten. Cast nickel-chromium-aluminium alloys have been proposed for this type of service and promising results have been obtained which make it

·probable that the use of this alloy may be extended in the future.

NON-FERROUS ALLOYS COMBINING OXIDATION-RESISTANCE WITH CORROSION-RESISTANCE

A large tonnage of non-ferrous metals and alloys are employed where a combination of resistance to scaling at elevated temperatures and resistance to corrosion are essential properties. An outstanding example of this class of application is the use of arsenical copper for locomotive fireboxes and stay rods. Other applications of a somewhat similar nature occur in the chemical and food industries, where metal is subject on one side to superheated steam or other hot gases, and to heated and more or less corrosive liquids on the other side.

In applications of this type it is rarely that the metal is subjected to temperatures in excess of 300° C., and resistance to scaling is normally less important than corrosion resistance, mechanical properties and ease of fabrication. Nevertheless in some types of equipment failure occasionally results from the development of an overheated area. Steam heating is, however, probably the most common method in the chemical and food industries, and in such cases scaling is not an important problem with any of the materials which are employed.

Where heating is obtained directly by the products of combustion of fuel, scaling is of more importance, and in the case of arsenical copper for locomotive fireboxes extensive research work has been carried out by Hudson, Herbert, Ball and Bucknall of the British Non-Ferrous Metals Research Association [16]. From a general study of the conditions prevailing in a locomotive firebox, and from the results of observations and tests made on locomotives in service, as well as the results of laboratory experimental work, the conclusion was reached that the wastage of stayheads, while primarily due to oxidation of the copper, is brought about by the action of water leaking between stays and plates. While dry, the oxide scale formed on copper in the firebox is hard and firmly adherent, but under the influence of leakage liquid, it becomes loose and readily detachable. The presence of about 0·47 per cent. of arsenic appears to exert little or no influence on the rate of oxidation of copper in pure dry air, but this element is necessary to give an adherent protective scale in a typical firebox atmosphere containing soot and smoke. During the

initial stages of its formation, the oxide scale is unusually permeable to oxygen, but it subsequently sinters to a more compact condition, and this is accompanied by a pronounced reduction in the rate of oxidation. This rate is influenced to a greater extent by temperature or the presence of small amounts of hydrochloric acid and sulphur dioxide than by small variations in the percentages of carbon dioxide, carbon monoxide or oxygen in the oxidising atmosphere.

Oxidation as a Means of Improving Surface Finish

Although the bulk of the non-ferrous metals and alloys used in industry oxidise rapidly in air at the temperatures employed for hot-working and annealing, thus leading to wastage of metal and the necessity for subsequent cleaning operations, advantage may, under certain circumstances, be taken of this scaling[2]. Only in exceptional circumstances is it possible to cast ingots entirely free from surface defects. In the case of heat-resisting materials it is common practice to machine the ingots in order to remove any defects which may be present, for otherwise blemishes might occur in the finished product. In the case of materials scaling freely in air, surface defects may be removed to a considerable extent by oxidation, thus rendering unnecessary the machining of the ingots. In this connection the type of scale which is formed and the adhesion of the scale to the metal is of the first importance. It is well known, for example, that copper of high purity develops an adherent scale in air, whereas phosphorus deoxidised copper, and copper containing small amounts of silver, lose their scales readily on quenching. It is known also that in the presence of certain materials such as bone ash or ammonium chloride the characteristics of the scale on copper are altered, and advantage of this is taken in the fabrication of copper.

There is no doubt that a large amount of information is available within the industries concerned regarding the factors involved in the scaling of non-ferrous metals and alloys, but very little information is to be found in published literature. A wide field for useful research lies in studies of the effect of impurities and additional elements on the scaling characteristics of non-ferrous alloys, both from the point of view of altering the amount of scale produced and in affecting the ease with which the scale can be removed.

BRIGHT ANNEALING

Although the scaling of some metals and alloys is frequently made use of in the early production stages, substantial advantages are generally obtained when scaling is prevented in the later stages of fabrication. The scale on metal seldom develops to a uniform thickness, while the pickling and other cleaning operations, which must be applied to oxidised surfaces, tend to destroy the smoothness and lustre of the product. Bright annealing generally results, not only in an improved product, but in a reduction of labour and in a simplification of the production line. This subject has been dealt with by Frith and by Hudson[8].

At the present time bright annealing operations are carried out successfully on copper, brass, bronze, nickel, copper-nickel alloys, nickel-silver and nickel-chromium alloys.

Electric heating is much used in connection with bright annealing equipment and a number of types of furnace have been described recently by Kloninger and others [7, 18, 20, 24]. Fuel fired furnaces are, however, also employed and, where the heat developed by the part combustion of the fuel is sufficient for the heating operations, such furnaces may be extremely economical.

The most commonly employed atmospheres for bright annealing operations are steam, hydrogen, nitrogen, hydrogen-nitrogen mixtures, producer gas, and partly burnt gases derived from butane or coal. In some places natural gas is employed, and occasionally annealing operations are carried out in vacuo. The choice of atmosphere depends mainly on the type of material to be annealed. It is important that the atmosphere should have no deleterious effects on the metal and that it should be simple and cheap to produce. In addition it is desirable, whenever possible, to have a non-explosive and non-poisonous gas.

A common difficulty with the atmospheres produced from partly burnt coal gas or producer gas is the presence of sulphur, and the increasing use of butane is due to the low-sulphur content of the atmosphere which can be obtained with the aid of this hydro-carbon. Some metals and alloys cannot be bright annealed in atmospheres containing steam or carbon dioxide, and for these hydrogen atmospheres and hydrogen-nitrogen atmospheres commonly obtained by the cracking or part combustion of ammonia are employed. Where nitrogen-

hydrogen mixtures are produced from partly burnt cracked ammonia, the water vapour is usually removed by cooling sometimes followed by desiccation over calcium chloride.

Copper may be annealed in a steam atmosphere in water-sealed furnaces, but it is important that the steam in the hot zone should be free from oxygen. A difficulty, however, with steam annealing of copper is the avoiding of water stains, but reducing atmospheres must be used with care owing to the danger of causing embrittlement or gassing. This defect is likely to develop in tough pitch copper when annealing operations are undertaken in atmospheres containing more than about 10 per cent. of reducing gases, particularly if the time is long and the temperature high.

A good deal of copper of certain grades is at the present time being annealed in nitrogen-hydrogen atmospheres containing about 5–8 per cent. hydrogen and produced by the controlled combustion of cracked ammonia. This type of atmosphere is expensive and can be used economically on copper only where the construction of the furnace is such that the gas consumption does not exceed 100–300 cubic feet per ton. In the case of continuous furnaces with open ends the gas consumption may amount to 1000–2000 cubic feet per ton, and a cheaper source of reducing atmosphere is necessary, such as that obtained by the controlling of the combustion of coal gas or butane to give an atmosphere containing about 88 per cent. nitrogen, 10 per cent. CO_2, and 2 per cent of reducing gases.

The bright annealing of brass is an operation more complicated than that of copper, owing to the volatility of zinc and its high affinity for oxygen. Volatilization of zinc is not serious when brass is annealed under oxidising conditions, but in reducing atmospheres substantial losses of zinc may occur, accompanied by loss of surface finish. Guillet [11] showed that 55/45 brass heated for 6 hours at 800° C. lost weight in air to the extent of about 1 per cent. while in carbon monoxide and in hydrogen the weight lost was nearly ten times as great. For the bright annealing of brass, therefore, special precautions must be taken to minimise the volatilization of zinc. This may be done by passing the gas over heated brass turnings or over hot zinc [15]. It has also been stated that the addition of methanol vapour to the furnace atmosphere leads to improved results [4, 6].

The bright annealing of nickel-silver is a somewhat similar

problem to that of brass, and attention has to be paid to the possibility of both oxidation and volatilization of the zinc. The problem is complicated not only by the varying zinc content of the commercial nickel-silvers but by the varying annealing temperatures which have to be used according to composition. Nickel-silvers are annealed successfully on a commercial scale in nitrogen-hydrogen mixtures, but attempts to carry out bright annealing operations in the cheaper atmospheres to be obtained by the controlled combustion of hydrocarbons has not in all cases proved successful and a good deal of further research work is necessary on this problem.

The bright annealing of nickel and nickel-copper alloys is a simple operation so far as the avoidance of oxidation is concerned. These alloys, however, are susceptible to surface deterioration when heated in reducing atmospheres containing sulphur compounds, and it is essential that the atmospheres used should be free from sulphur. Even town's gas contains too much sulphur for satisfactory working, and a good deal of attention has been given to the possibilities of developing an economical process for lowering the sulphur content of town's gas. Developments in this direction may be expected in the future, since town's gas is likely to be a cheaper source of a reducing atmosphere than butane or ammonia. At the present time satisfactory results are being obtained with these alloys with the aid of butane and partly burnt cracked ammonia.

The bright annealing of nickel-chromium alloys is a difficult operation. There is a tendency for bright annealed nickel-chromium alloy electrical-resistance wire to be employed in preference to open annealed wire, although there do not appear to be any important advantages to be gained by making this change. In the drawing process, however, bright annealing has advantages over open annealing because of the difficulty of pickling nickel-chromium alloys. Bright annealing nickel-chromium alloys in containers has not yet been made a commercial success, but satisfactory results have been obtained in continuous annealing where strands of wire pass continuously through a tube-type furnace heated to a temperature of about 1100° C. and filled with an atmosphere of hydrogen or hydrogen-nitrogen mixture. The essential features for success in this operation are substantially complete absence of oxygen, free or combined, a high annealing temperature, and rapid cooling.

While complete absence of oxygen is not essential to avoid oxidation at temperatures over 1000°C., high purity in the atmosphere or rapid cooling is essential if the development of oxide films is to be avoided at lower temperatures.

Close annealing operations, so much employed in the steel trade, are also used in the non-ferrous industry in the annealing of copper and nickel. Advantage is taken of the reducing atmosphere, which results from the decomposition and volatilization of oil or grease on the metal, to drive out the air and prevent oxidation. In some cases, however, charcoal is introduced into the box to assist in the maintenance of reducing conditions. In some types of furnace the container is provided with a non-return valve which allows gases to escape on heating, but prevents the entrance of air on cooling. In some cases also hydrogen steam mixtures or other gases are passed into the box during the annealing operation, but more particularly during cooling.

Liquid salt baths are used to some extent in non-ferrous trades, particularly in the annealing of silver and nickel-silver. This type of annealing may develop in the future, but a good deal of research is required to bring out the most suitable salt mixtures for the various alloys.

Broadly speaking, the bright annealing problem centres round the most economical processes for the development of suitable atmospheres, and a wide field for research exists calling for co-operation between the chemist, the metallurgist, and electrical and fuel engineers. Much research has already been carried out on the equilibrium relationships between metal oxides and various gases, but much more remains to be done, especially perhaps in connection with alloys containing elements having a high affinity for oxygen and elements liable to volatilize at the annealing temperatures.

Minor Applications for Non-Ferrous Heat-Resisting Alloys

Reference must be made to some applications which, although consuming only small tonnages of non-ferrous alloys are nevertheless of considerable technical importance.

In modern internal combustion engines, particularly in aero engines, valve seat inserts are commonly made from aluminium-bronze, nickel-copper alloys, and stellite, since

these materials combine suitable mechanical properties at elevated temperatures with oxidation and corrosion resistance. Non-ferrous alloys are also used for valve parts in steam and other branches of engineering. A considerable amount of research has already been carried out in connection with materials for applications such as these. Oxidation resistance is not, of course, the only important characteristic of suitable alloys, and factors such as coefficient of expansion and resistance to galling must be taken into account.

Aluminium bronzes have been found useful for the construction of burner parts of gas lighting installations, and no doubt the aluminium brasses [9] have similar fields of usefulness. Aluminium as an alloying constituent has been found effective where resistance to attack by sulphur gases is concerned [10].

Some mention should also be made of the non-ferrous alloys used in steam turbine construction. Suitable alloys for turbine blades must possess good mechanical properties combined with resistance to attack by steam. The tip speed of blades may reach 550 feet per second involving high stresses, while temperatures exceeding 350°C. are likely in the near future. In the high pressure stages, nickel-copper alloy blades are in extensive use owing to the combination of high strength, resistance to attack by steam, and ease of fabrication possessed by these alloys. In the low pressure stages, strength at ordinary temperatures combined with resistance to corrosion by wet steam are essential requirements, and a variety of brasses as well as nickel-copper alloys are used for the blades. There seems no reason to suppose that the conditions in steam turbines will not become increasingly severe and much attention could usefully be directed to the improvement of existing alloys and the development of new materials for this application.

Base metal thermocouples are required not only to have suitable thermo-electric characteristics, but to possess also a considerable degree of scaling resistance. In the lower temperature ranges satisfactory results are obtained with copper and nickel-copper alloys as couples, while in the higher temperature ranges the most commonly used couple consists of nickel-chromium and nickel-aluminium alloys.

Lead-in wires for electrical heating equipment are not infrequently made from pure nickel, this material being employed because it combines heat-resistance with a rela-

tively high electrical conductivity and suitable mechanical properties.

The scaling resistance of many ferrous and ·non-ferrous alloys may be improved by surface treatments that produce a protective covering of aluminium, e.g., calorising and spraying with aluminium. Treatments of this kind are used to prolong the life of boiler tubes and other furnace parts. A somewhat similar method of protection consists of subjecting articles to a cementation process which develops an aluminium-rich alloy at the surface.[5, 14, 21] When this process is carried out under suitable conditions a skin is produced which has a high melting point and a high resistance to scaling, and although the skin is brittle, the use of a satisfactory metal for the core provides a serviceable article. In recent years a good deal of attention has been devoted to improving this method of producing heat-resisting parts, and proposals have been made for developing heat-resistance by forming a surface deposit in which aluminium is combined with other elements such as chromium and nickel.

Information which has been acquired in recent years on the subject of creep at elevated temperatures has led to the view being commonly expressed that the future demands of engineering will involve the increasing use of hard and non-ductile alloys in the form of castings, where a minimum degree of distortion at elevated temperatures is an essential requirement. Increasing interest has, therefore, become centred round alloys of the intermetallic compound type, many of which have a high melting point and possess an extremely high resistance to oxidation and corrosion.

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